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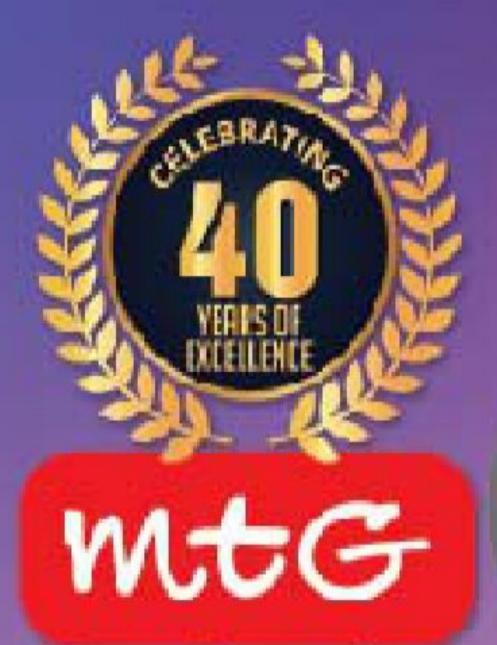
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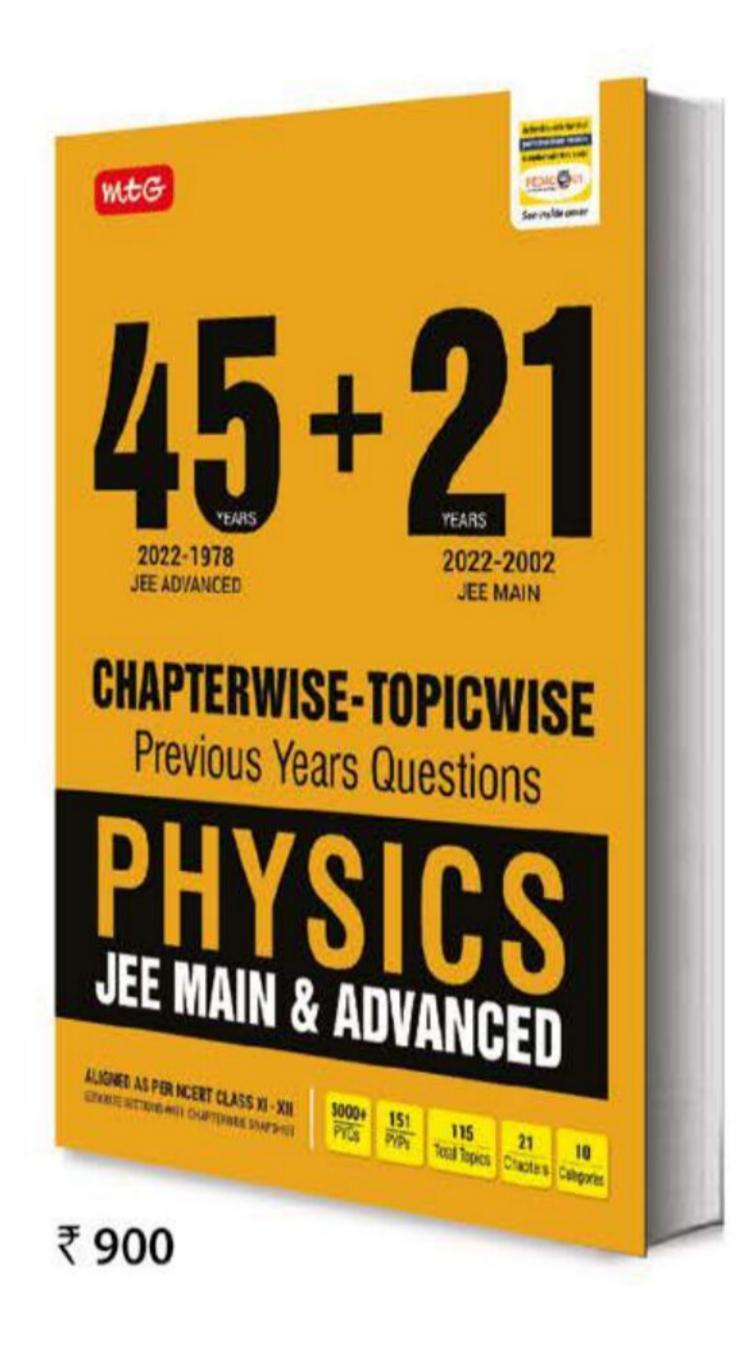
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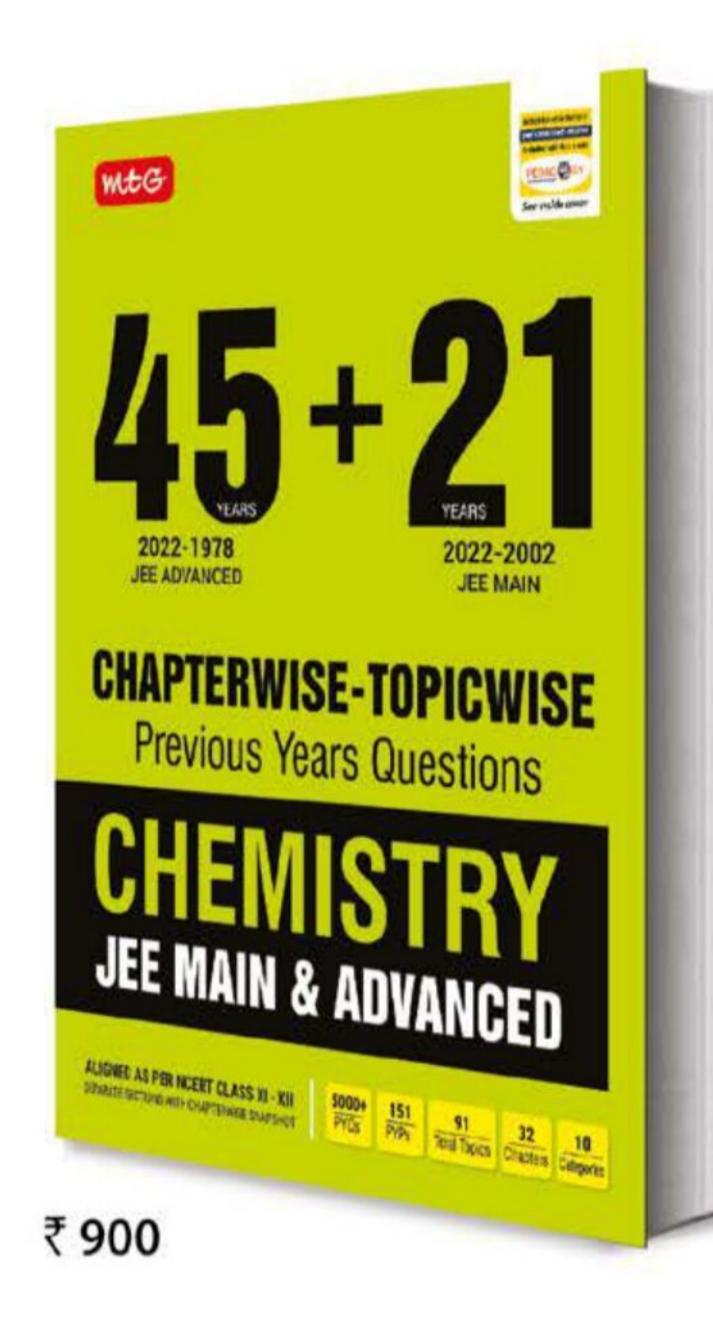


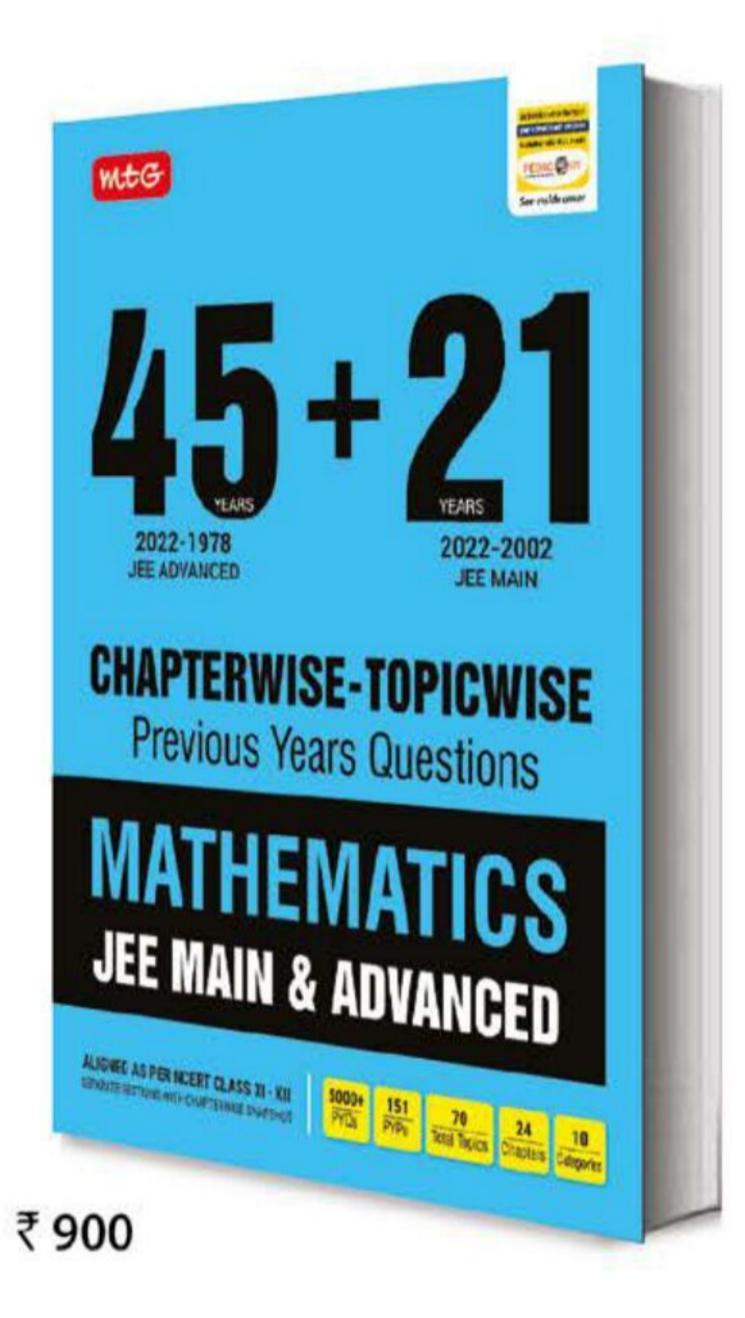
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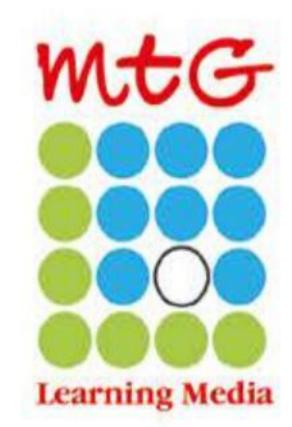




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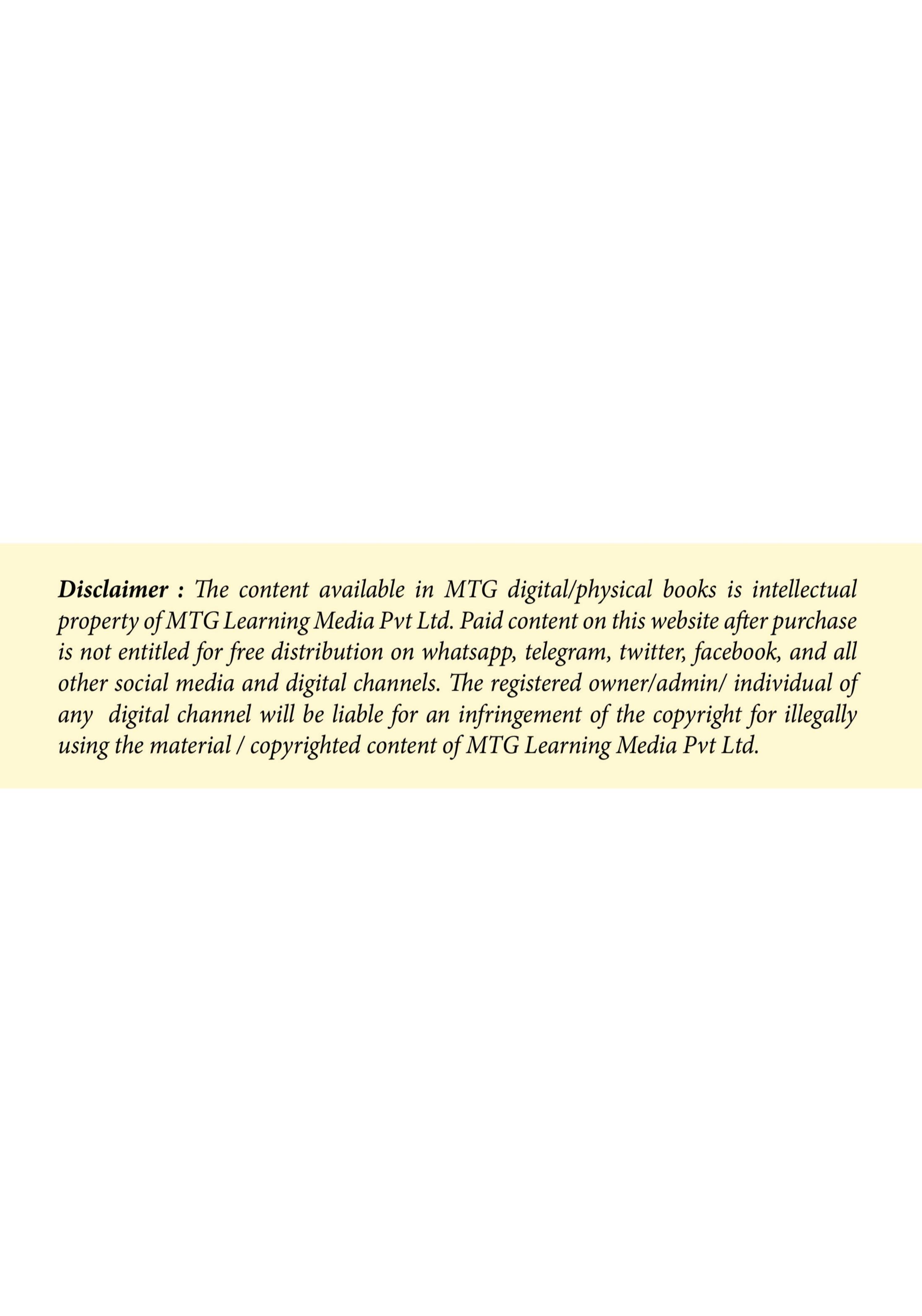
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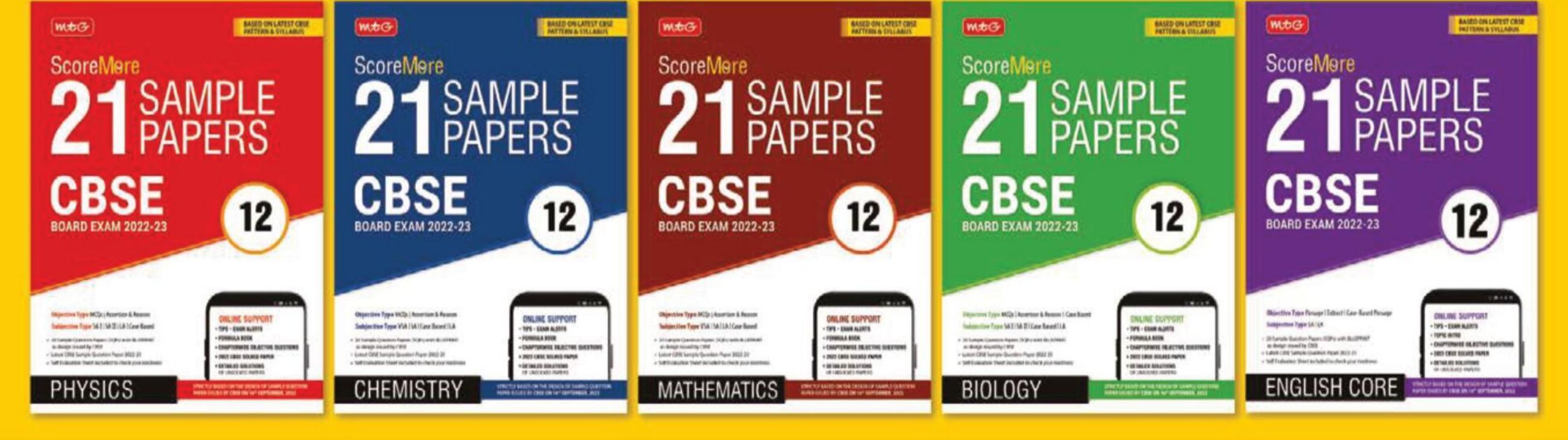
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# CHEMISIRY

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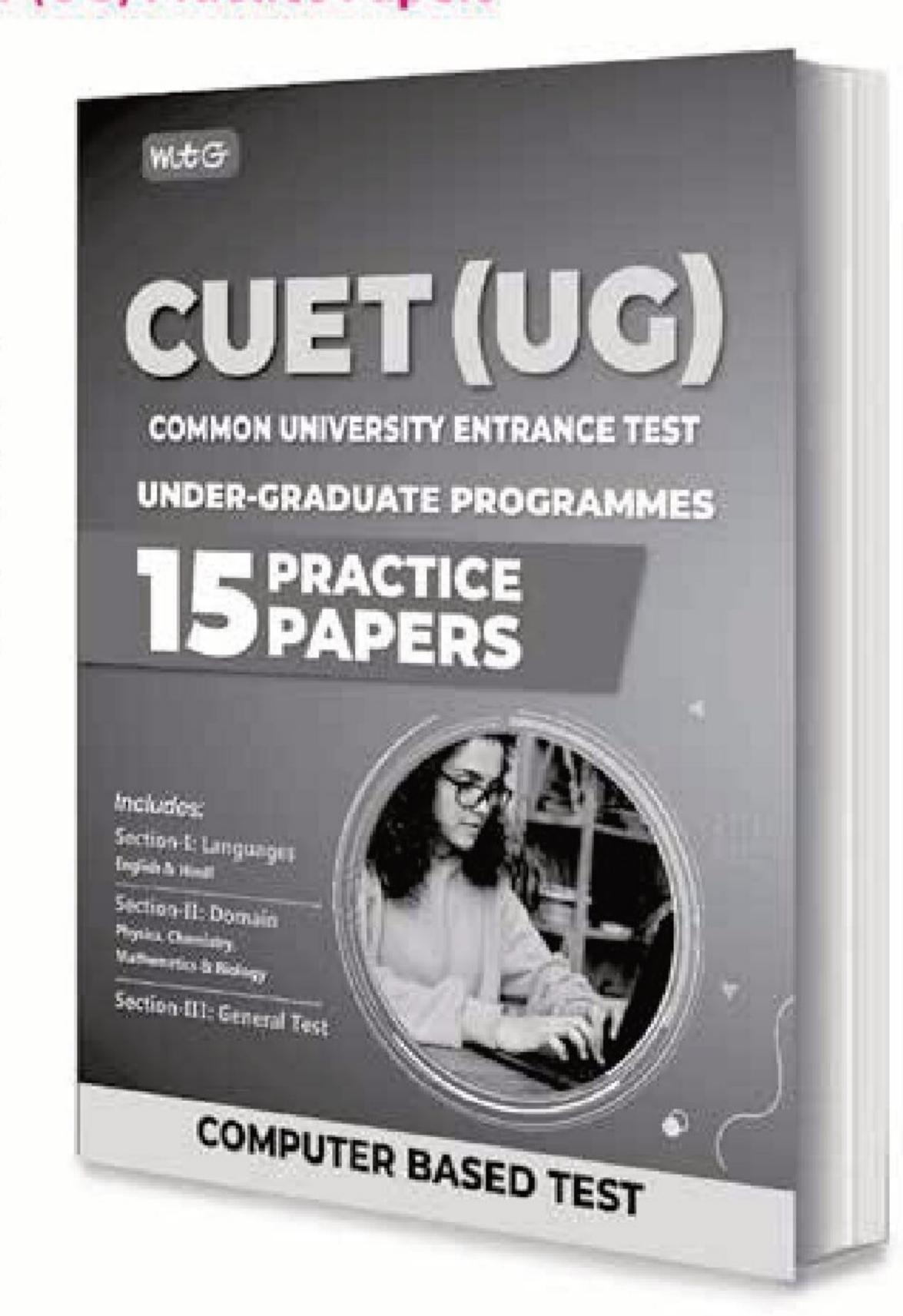
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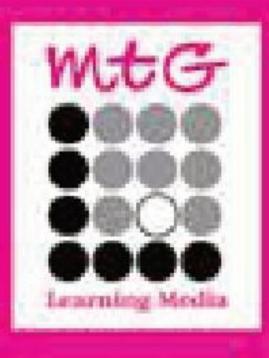
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### CHAPTERWISE PRACTICE PAPER 2023

# CUET (UG)

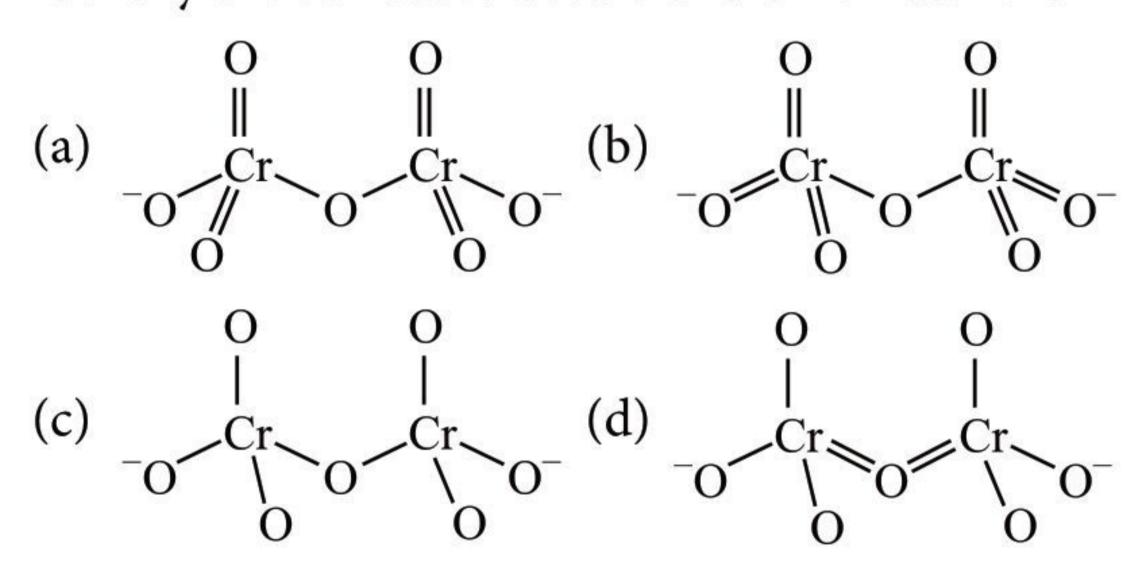
#### The *p*-Block Elements | The *d*- and *f*-Block Elements

Section II of CUET (UG) is domain specific. In this section of Chemistry 40 questions to be attempted out of 50.

Maximum Marks: 200 Time Allowed: 45 Minutes

#### Multiple Choice Questions (MCQs)

- The number of P = O and P-O-H bonds in  $H_3PO_4$ are respectively
  - (a) 3, 1
- (b) 2, 2
- (c) 1, 2
- (d) 1, 3
- Choose the correct statement for transition elements.
  - (a) Transition elements have low melting points.
    - (b) Transition elements do not have catalytic activity.
    - (c) Transition elements exhibit variable oxidation states.
    - (d) Transition elements exhibit inert pair effect.
- The decreasing order of boiling points of the following hydrides is
  - (a)  $SbH_3 > AsH_3 > PH_3 > NH_3$
  - (b)  $NH_3 > SbH_3 > AsH_3 > PH_3$
  - (c)  $SbH_3 > NH_3 > AsH_3 > PH_3$
  - (d)  $PH_3 > AsH_3 > SbH_3 > NH_3$
- Identify the correct structure of dichromate ion.



- Which of the following statements about noble gases is false?
  - (a) They are used to provide inert atmosphere in many chemical reactions.
  - (b) They are only sparingly soluble in water.
  - (c) They form diatomic molecules.
  - (d) Some of them are used to fill discharge tubes used for advertising signs.

- Among the following ions:
  - (i)  $Cu^{2+}$  (ii)  $Ti^{4+}$
- (iii) Co<sup>2+</sup>
- (iv) Fe<sup>2+</sup>

The coloured ions are

- (a) (i), (ii), (iii), (iv)
- (b) (i), (iii), (iv) only
- (c) (ii), (iii) only
- (d) (ii), (iv) only.
- Select the correct option regarding the properties of dioxygen?
  - (a) Dioxygen never reacts with metals.
  - (b) Dioxygen is diamagnetic in nature.
  - (c) Combination of dioxygen with other elements is a highly exothermic process.
  - (d) Dioxygen liquefies at 55 K and freezes at 90 K.
- For the oxides of manganese, select the correct increasing order of acidic strength.
  - (a)  $MnO < Mn_3O_4 < Mn_2O_3 < MnO_2 < Mn_2O_7$
  - (b)  $Mn_2O_7 < MnO_2 < Mn_2O_3 < Mn_3O_4 < MnO_3$
  - (c)  $MnO_2 < Mn_2O_7 < Mn_3O_4 < Mn_2O_3 < MnO$
  - (d)  $Mn_3O_4 < Mn_2O_3 < Mn_2O_7 < MnO_2 < MnO_3$
- A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and halate respectively are
  - (a) Br<sub>2</sub> and KBrO<sub>3</sub>
- (b) Cl<sub>2</sub> and KClO<sub>3</sub>
- (c) I<sub>2</sub> and NaIO<sub>3</sub>
- (d) Cl<sub>2</sub> and NaClO<sub>3</sub>.
- 10. When SO<sub>2</sub> is passed through acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution,
  - (a) the solution turns blue
  - (b) the solution is decolourised
  - (c) SO<sub>2</sub> is reduced
  - (d) green  $Cr_2(SO_4)_3$  is formed.
- 11. In which of the following sulphur is present in +5 oxidation state?
  - (a) Dithionic acid
- (b) Sulphurous acid
- (c) Sulphuric acid
- (d) Disulphuric acid

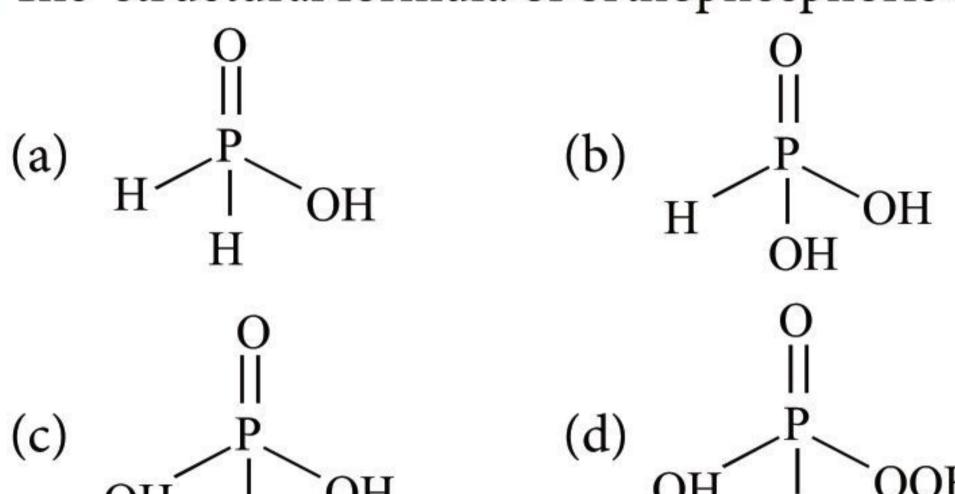
12. Which of the following lanthanoid ions is paramagnetic? (a)  $Ce^{4+}$  (b)  $Yb^{2+}$  (c)  $Lu^{3+}$  (d)  $Eu^{2+}$ 

- 13. When three parts of conc. HCl and one part of conc. HNO<sub>3</sub> is mixed, a compound 'X' is formed. The correct option related to 'X' is
  - (a) 'X' is known as aqua-regia
  - (b) 'X' is used for dissolving gold
  - (c) 'X' is used for decomposition of salts of weaker acids
  - (d) both (a) and (b).
- **14.** The general configuration of *f*-block elements is
  - (a)  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$
  - (b)  $(n-1)f^{1-14}(n-1)d^{0-1}ns^2$
  - (c)  $(n-3)f^{1-14}(n-2)d^{0-1}(n-1)s^2$
  - (d)  $(n-2)f^{0-1}(n-1)d^{0-1}ns^2$
- 15. In the reaction,

 $HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + X$ , the product X is

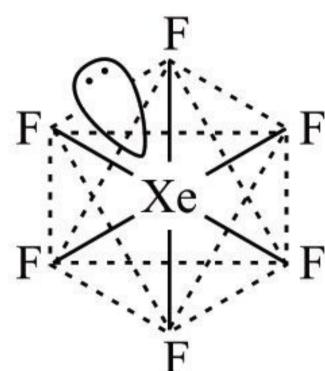
- (a)  $N_2O_5$  (b)  $H_2O$  (c)  $NO_2$
- 16. Which of the following is the most basic?
  - (a)  $Ce(OH)_3$
- (b)  $Lu(OH)_3$
- (c)  $Yb(OH)_3$
- $(d) Tb(OH)_3$
- 17. Which of the following statements is not correct about the structure of PCl<sub>5</sub>?
  - (a) PCl<sub>5</sub> has a trigonal bipyramidal structure.
  - (b) The three equatorial P–Cl bonds are equivalent.
  - (c) The two axial bonds are different and longer than equatorial bonds.
  - (d) Equatorial bond pairs suffer more repulsion than axial bond pairs.
- 18. Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect?
  - (a) The common oxidation states of cerium are +3 and +4.
  - (b) The +3 oxidation state of cerium is more stable than +4 oxidation state.
  - (c) The +4 oxidation state of cerium is not known in solutions.
  - (d) Cerium (IV) acts as an oxidising agent.
- 19. Name of the synthetic radioactive element of group 16 having atomic number 116 is
  - (a) Livermorium
- (b) Tennessine
- (c) Flerovium
- (d) Moscovium.
- 20. Which of the following reactions is not correct?
  - (a)  $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
  - CHEMISTRY TODAY DECEMBER '22

- (b)  $2MnO_2 + 4KOH + O_2 \rightarrow 4KMnO_4 + 2H_2O$
- (c)  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$
- (d)  $K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow$  $4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$
- 21. The structural formula of orthophosphoric acid is



- 22. An explosion takes place when conc. H<sub>2</sub>SO<sub>4</sub> is added to KMnO<sub>4</sub>. Which of the following compounds is formed?
  - (a)  $Mn_2O_7$  (b)  $MnO_2$  (c)  $MnSO_4$  (d)  $Mn_2O_3$
- 23. Which of the following increasing order is not correct as mentioned in the property with it?
  - (a)  $HClO_2 < HClO_3 < HClO_4 : (thermal)$ stability)
  - (b)  $HClO_4 < HClO_3 < HClO_2 < HClO : (oxidising)$ power)
  - (c)  $F^- < Cl^- < Br^- < I^-$ : (reducing nature)
  - (d)  $HIO_4 < ICl < I_2 < HI : (oxidation number of$ iodine)
- 24. Which of the following statements concerning lanthanoid elements is false?
  - (a) Lanthanoids are separated from one another by ion-exchange method.
  - (b) Ionic radii of trivalent lanthanoids steadily increase with increase in the atomic number.
  - (c) All lanthanoids are highly dense metals.
  - (d) Most characteristic oxidation state of lanthanoid elements is +3.
- 25. In XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>, the number of lone pairs on Xe is respectively
  - (a) 2, 3 and 1
- (b) 1, 2 and 3
- (c) 4, 1 and 2
- (d) 3, 2 and 1
- 26. For Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Cr<sup>2+</sup>, which of the following statements is correct?
  - (a) Only Zn<sup>2+</sup> is colourless and Ni<sup>2+</sup>, Cu<sup>2+</sup> and Cr<sup>2+</sup> are coloured.
  - (b) All the ions are coloured.
  - (c) All the ions are colourless.
  - (d) Zn<sup>2+</sup> and Cu<sup>2+</sup> are colourless while Ni<sup>2+</sup> and Cr<sup>2+</sup> are coloured.

- 27. Which of the following has +4 oxidation state?
  - (a)  $H_3PO_4$
- (b)  $H_3PO_3$
- (c)  $H_4P_2O_7$
- (d)  $H_4P_2O_6$
- 28. The correct order of decreasing second ionisation enthalpy of Ti(22), V(23), Cr(24) and Mn(25) is
  - (a) Mn > Cr > Ti > V (b) Ti > V > Cr > Mn
- - (c) Cr > Mn > V > Ti (d) V > Mn > Cr > Ti
- 29. Which of the following is not correct about xenon hexafluoride?



- (a) Xe has an oxidation state of +6.
- (b) The hybridisation involved in  $XeF_6$  is  $sp^3d^3$ .
- (c) The shape of XeF<sub>6</sub> is distorted octahedral and can be represented as above.
- (d) On hydrolysis, it gives Xe, HF and  $O_2$ .
- 30. The magnetic moment of a divalent ion in aqueous solution with atomic number 25 is
  - (a) 5.9 B.M. (b) 2.9 B.M. (c) 6.9 B.M. (d) 9.9 B.M.
- 31. Which of the following is a tetrabasic acid?
  - (a) Hypophosphorous acid
  - (b) Metaphosphoric acid
  - (c) Pyrophosphoric acid
  - (d) Orthophosphoric acid
- 32. Select the correct option regarding Sc(III), Ti(IV), Pd(II) and Cu(II) ions.
  - (a) All are paramagnetic.
  - (b) All are diamagnetic.
  - (c) Sc(III) and Ti(IV) are paramagnetic while Pd(III) and Cu(II) are diamagnetic.
  - (d) Sc(III) and Ti(IV) are diamagnetic while Pd(II) and Cu(II) are paramagnetic.
- 33. Identify the correct sequence of increasing number of  $\pi$ -bonds in structures of the following molecules.
- I.  $H_2S_2O_6$  II.  $H_2SO_3$  III.  $H_2S_2O_5$
- (a) I, II, III
- (b) II, III, I
- (c) II, I, III
- (d) I, III, II
- **34.** Gadolinium belongs to 4*f* series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?
  - (a) [Xe]  $4f^75d^16s^2$
- (b) [Xe]  $4f^65d^26s^2$
- (c) [Xe]  $4f^86d^2$
- (d) [Xe]  $4f^95s^1$

#### **Assertion & Reason Based MCQs**

For question numbers 35-38, a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

- If both assertion and reason are correct and reason is the correct explanation of assertion.
- If both assertion and reason are correct but reason is not the correct explanation of assertion.
- If assertion is correct but reason is wrong.
- If assertion is wrong but reason is correct.
- 35. Assertion: White phosphorus is more reactive than red phosphorus.

Reason: White phosphorus readily catches fire in air to give dense white fumes of  $P_4O_{10}$ .

**36. Assertion**: Magnetic moment of Mn<sup>2+</sup> is less than that of  $Cr^{2+}$ .

Reason: The transition elements exhibit catalytic properties due to their ability to show variable oxidation states.

37. Assertion: Acidic character of group 16 hydrides increases from  $H_2O$  to  $H_2Te$ .

Reason: Thermal stablility of hydrides decreases down the group.

38. Assertion: Zr and Hf occur together in nature and are difficult to separate.

Reason: Zr and Hf have identical radii due to lanthanoid contraction.



The same THREE LETTERS will complete these five words.

Can you find the three-letter sequence?

DENA - - ATION

SA - - ATED

STRUC - - E

TINC - - E

NOMENCLA - - E

Readers can send their responses at editor@mtg.in or post us with complete address by 10<sup>th</sup> of every month. Winners' names will be published in next issue.

#### **Match the Columns**

39. Match the Column I with Column II and mark the appropriate choice.

	Column I		Column II
(A)	$H_2SO_3$	(i)	+6, dibasic
(B)	$H_2SO_5$	(ii)	+5, dibasic
(C)	$H_2S_2O_6$	(iii)	+6, monobasic
(D)	$H_2SO_4$	(iv)	+4, dibasic

(a) (A) 
$$\rightarrow$$
 (i); (B)  $\rightarrow$  (ii); (C)  $\rightarrow$  (iii); (D)  $\rightarrow$  (iv)

(b) (A) 
$$\rightarrow$$
 (ii); (B)  $\rightarrow$  (iii); (C)  $\rightarrow$  (i); (D)  $\rightarrow$  (iv)

(c) (A) 
$$\rightarrow$$
 (iii); (B)  $\rightarrow$  (iv); (C)  $\rightarrow$  (ii); (D)  $\rightarrow$  (i)

(d) (A) 
$$\rightarrow$$
 (iv); (B)  $\rightarrow$  (iii); (C)  $\rightarrow$  (ii); (D)  $\rightarrow$  (i)

40. Match the Column I with Column II and mark the appropriate choice.

	Column I	Column II		
(A)	Element with highest second ionisation enthalpy	(i)	Cr	
(B)	Element with highest third ionisation enthalpy	(ii)	Cu	
(C)	$M \text{ in } M(CO)_6 \text{ is}$	(iii)	Zn	
(D)	Element with highest heat of atomisation	(iv)	Ni	

(a) 
$$(A) \to (iv), (B) \to (i), (C) \to (ii), (D) \to (iii)$$

(b) (A) 
$$\to$$
 (iii), (B)  $\to$  (iv), (C)  $\to$  (ii), (D)  $\to$  (i)

(c) 
$$(A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (i), (D) \rightarrow (iv)$$

(d) (A) 
$$\rightarrow$$
 (i), (B)  $\rightarrow$  (ii), (C)  $\rightarrow$  (iv),(D)  $\rightarrow$  (iii)

#### **Case Based MCQs**

#### Case I: Read the passage given below and answer the following questions from 41 to 45.

Potassium permanganate is prepared from pyrolurite which is an oxide of manganese. Pyrolusite is fused with KOH or K<sub>2</sub>CO<sub>3</sub> in the presence of air or some oxidating agent. The fused mass is extracted with water and filtered to get a green solution. When chlorine gas is passed through the green solution, the colour of the solution changes to purple due to formation of  $KMnO_4$ .

#### The following questions are multiple choice questions. Choose the most appropriate answer:

- 41. The formula of pyrolusite is
  - (a)  $Mn_3O_4$

(b)  $MnO_2$ 

(c) MnO

(d)  $Mn_2O_7$ 

- CHEMISTRY TODAY DECEMBER '22

- **42.** The green solution contains
  - (a)  $KMnO_4$
- (b)  $Mn_3O_4$
- (c)  $K_2MnO_4$
- (d)  $K_2MnO_3$
- 43. When chlorine gas is passed through green solution, the oxidation no. of Mn changes from
  - (a) 6 to 7

(b) 4 to 7

(c) 4 to 6

(d) 7 to 4

- **44.** The purple colour of KMnO₄ is due
  - (a) d-d transition
- (b) charge transfer
- (c) p-d transition
- (d) d-p transition
- **45.** The hybrid state of Mn in KMnO₄ is
  - (a)  $sp^3d$
- (b)  $sp^2$
- (c)  $sd^3$
- (d)  $sp^3d^2$

#### Case II: Read the passage given below and answer the following questions from 46 to 50.

Group 17 elements are known as halogens (sea-salt forming). Their general electronic configuration is  $[ns^2np^5]$ . Flourine, the first member of the group, differs in several ways from the rest of the group. Halogens are highly reactive elements having strong affinity for hydrogen. All the halogen acids have low boiling points.

#### The following questions are multiple choice questions. Choose the most appropriate answer:

- 46. The oxidising power of halogens is of the order,

  - (a)  $F_2 > I_2 > Br_2 > Cl_2$  (b)  $F_2 > Cl_2 > Br_2 > I_2$
  - (c)  $I_2 > Br_2 > Cl_2 > F_2$  (d)  $Cl_2 > F_2 > Br_2 > I_2$



- 47. The property of halogens which is not correctly matched is
  - (a) F > Cl > Br > I: (Ionisation energy)
  - (b) F > Cl > Br > I : (Electronegativity)
  - (c) I > Br > Cl > F : (Density)
  - (d) F > Cl > Br > I: (Electron affinity)
- 48. What is the correct arrangement of the compounds based on their decreasing bond strength?
  - (a) HF > HCl > HBr > HI
  - (b) HI > HBr > HCl > HF
  - (c) HCl > HF > HBr > HI
  - (d) HF > HBr > HCl > HI
- 49. Mark the correct statement about halogens.
  - (a) Electron affinity of halogens is of the order, F > Cl > Br > I.
  - (b) HF is the strongest hydrohalic acid.
  - (c)  $F_2$  has lower bond dissociation energy than  $Cl_2$ .
  - (d) All halogens show variable oxidation states.
- 50. The element of group 17 whose half-life is in milliseconds only is
  - (a) Ts
- (b) Te
- (c) At
- (d) Og

#### **SOLUTIONS**

- 2. (c): Transition elements exhibit variable oxidation states.
- 3. (c): NH<sub>3</sub> has abnormally high boiling point because of its tendency to form hydrogen bonds. NH<sub>3</sub> has higher boiling point than phosphine and then boiling point increases down the group because of increase in size. Hence, the order of boiling point will be

$$SbH_3 > NH_3 > AsH_3 > PH_3$$

- (a)
- (c): Noble gases exist as monoatomic gases.
- 6. (b)
- 7. (c)
- (a): Acidic strength of oxides of transition metals increases with increase in oxidation number.

Hence, acidic strength is of the order of

$$\mathrm{MnO} < \mathrm{Mn_3O_4} < \mathrm{Mn_2O_3} < \mathrm{MnO_2} < \mathrm{Mn_2O_7}$$
 $\mathrm{Amphoteric}$ 
Acidic

9. (b): A halate will be formed from halogen and the greenish yellow gas is Cl<sub>2</sub>. The halate which is used in fireworks and safety matches is KClO<sub>3</sub>. The reaction involved is

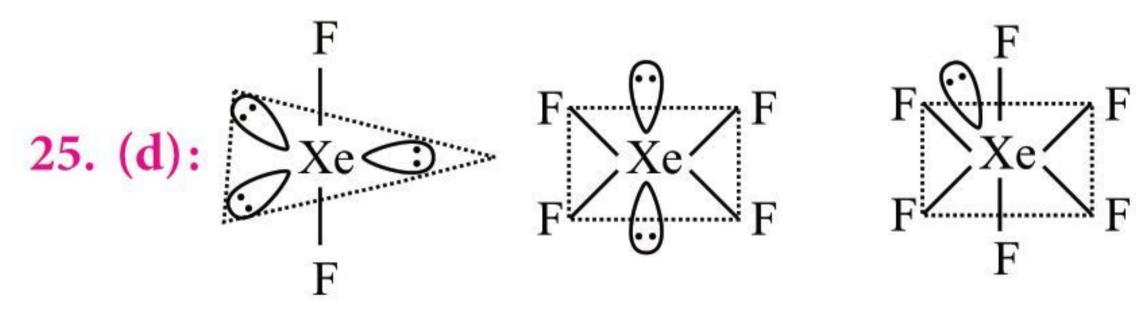
$$3Cl_2 + 6KOH \longrightarrow KClO_3 + 5KCl + 3H_2O$$
  
Greenish  
yellow gas

10. (d): 
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
 (green)

13. (d): 
$$3HCl_{(conc.)} + HNO_{3(conc.)} \longrightarrow HNO_3$$
.  $3HCl_{(X)}$ 

Aqua regia is used for dissolving noble metals like gold and platinum. HCl decomposes salts of weaker acids e.g., carbonates, hydrogen carbonates, sulphites, etc.

- 14. (a)
- 15. (a):  $4\text{HNO}_3 + P_4O_{10} \rightarrow 4\text{HPO}_3 + 2N_2O_5$ Nitrogen pentoxide can be formed by heating P<sub>4</sub>O<sub>10</sub> with conc. nitric acid.
- 16. (a)
- 17. (d): The axial bond pairs suffer more repulsion as compared to equatorial bond pairs.
- 18. (c): The +4 oxidation state of cerium is also known in solutions.
- 19. (a)
- 20. (b):  $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$
- 21. (c): Orthophosphoric acid is H<sub>3</sub>PO<sub>4</sub>.
- 22. (a):  $2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Mn_2O_7 + H_2O$ (Explosive)
- 23. (d): Increasing oxidation number of iodine is in the order :  $HI < I_2 < ICl < HIO_4$
- 24. (b): The ionic radii of lanthanoid elements decrease steadily with increase in atomic number due to lanthanoid contraction.



26. (a):  $Zn^{2+}(3d^{10})$  has zero unpaired electron (colourless).

 $Ni^{2+}(3d^8)$  has 2 unpaired electrons (coloured).

 $Cu^{2+}(3d^9)$  has 1 unpaired electron (coloured).

 $Cr^{2+}(3d^4)$  has 4 unpaired electrons (coloured).

27. (d) 2

29. (d): On hydrolysis of xenon hexafluoride, the products formed are XeO<sub>3</sub> and HF.

 $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$ 

30. (a) 31. (c)

32. (d): Sc(III) and Ti(IV) do not have unpaired electrons, thus these two are diamagnetic.

33. (b) 34. (a)

35. (b): White phosphorus is less stable and more reactive than red phosphorus because of angular strain in the  $P_4$  molecule where the angles are only 60°.

36. (d)

37. (b): The acidic character increases down the group and thermal stability of hydrides decreases down the group due to decrease in bond (H-E) dissociation enthalpy down the group.

38. (a) 39. (d) 40. (c)

41. (b): Pyrolusite is MnO<sub>2</sub>.

**42.** (c): Green coloured compound is potassium manganate, K<sub>2</sub>MnO<sub>4</sub>.

43. (a):  $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$ The oxidation no. of Mn in  $K_2MnO_4$  is +6 while in  $KMnO_4$ , it is +7.

**44. (b)**: The colour of KMnO<sub>4</sub> is due to charge transfer as Mn in +7 oxidation state and do not have any *d*-electron.

45. (c):  $KMnO_4$  is tetrahedral with Mn in  $sd^3$ -hybrid state.

46. (b)

47. (d): Electron affinity of Cl is maximum. The correct trend is Cl > F > Br > I.

48. (a)

49. (c):  $F_2$  has lower bond dissociation energy than  $Cl_2$  due to its small size which results in interelectronic repulsions.

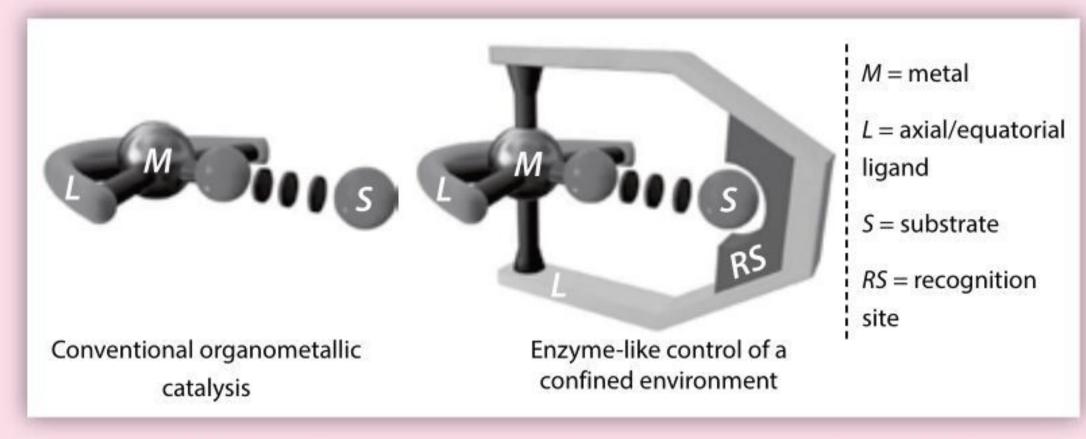
50. (a)



### CHEMISTRY BULLETIN

#### Designer catalyst with enzyme-like cavity splits water almost as fast as plants!

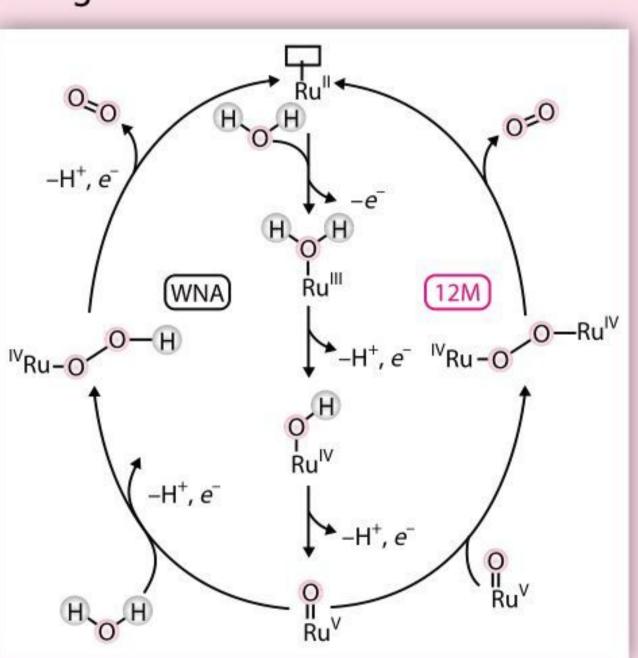
Using molecular design, researchers have developed a synthetic water oxidation catalyst with an enzyme-like cavity to speed up the reaction. This unusual catalytic system achieves the challenging oxidative water-splitting reaction at a comparable rate to the photosystems found in photosynthesis.



Water oxidation is a key step in photosynthesis and involves splitting of two water molecules into molecular oxygen and protons using solar energy. While this process is crucial in nature to sustain life, the ability to reproduce this reaction cheaply could help meet humanity's energy needs by creating a steady stream of oxygen and hydrogen. Synthetic mimics of the natural oxygen evolving complex are known, but generally suffer from low catalytic activity or short lifetimes. 'It is very hard to oxidise water,' explains a renewable energy chemist. 'The process requires the transfer of four electrons and so needs a lot of electrochemical or photochemical energy. One of the particularly tricky aspects is ensuring that the catalyst isn't just "burnt up" by these demanding conditions.'

Ruthenium metal centres have shown promise as water oxidation catalysts, but their performance is strongly dependent on the mechanistic pathway of the oxygen-oxygen bond forming reaction. Altering pH can promote preorganisation of water molecules around the metal centre, favouring the water nucleophilic attack mechanism and resulting in enhanced catalytic performance. However, this has been rarely used in catalyst design.

Researchers in Germany have now developed a pH-sensitive macrocyclic ruthenium system, able to form an enzyme-like cavity around the metal acidic under centre conditions. 'Traditional transition metal catalyst design focused has on the directly bound ligands to tune electronic properties and



structural environment,' says an organic chemist. 'Here we have embedded the ruthenium catalyst in a macrocycle to make use of the functional groups positioned on the opposite side of the pocket.' Extensive mechanistic analysis revealed that the macrocycle acts like a pH-controlled door, closing to form a small molecular cleft under acidic conditions. At low pH, the basic groups on the backbone of the macrocycle become protonated, resulting in the slight rotation of the axial ligands. This creates an enclosed enzyme-like cavity in which hydrogen bonds preorganise molecules of water in front of the reactive ruthenium centre, enabling rapid oxidation.

# Are you ready for Olympiads

#### LEVEL II





#### **SYLLABUS**\*

**Section** – **1**: *Physics*: Units and Measurements, Mechanics, Properties of Matter, Heat and Thermodynamics, Oscillations, Waves.

Chemistry: Some Basic Concepts of Chemistry, Structure of Atom, Classification of Elements and Periodicity in Properties, Chemical Bonding and Molecular Structure, States of Matter, Thermodynamics, Equilibrium, Redox Reactions, Hydrogen, The s-Block Elements, The p-Block Elements (Groups 13 and 14), Organic Chemistry - Some Basic Principles and Techniques, Hydrocarbons, Environmental Chemistry.

**Section – 2**: Higher Order Thinking Questions - Syllabus as per Section -1.

CLASS XI

Total Questions: 50 Time: 1 hr.

	PATTERN & MA	RKING SCHEME	
Section	(1) Physics & Chemistry	(2) Achievers Section	(3) Mathematics or Biology
No. of Questions	25	5	20
Marks per Ques.	1	3	1

**Section – 3**: Sets, Relations and Functions, Principle of Mathematical Induction, Logarithms, Complex Numbers & Quadratic Equations, Linear Inequations, Sequences and Series, Trigonometry, Straight Lines, Conic Sections, Permutations and Combinations, Binomial Theorem, Statistics, Mathematical Reasoning, Limits and Derivatives, Probability, Introduction to 3-D Geometry.

OR

Section – 3: Diversity in the Living World, Structural Organisation in Plants and Animals, Cell: Structure and Functions, Plant Physiology, Human Physiology.

#### **Practice Questions**

- 1. At 300 K,  $N_2$  and  $H_2$  are mixed and the reaction,  $N_2 + 3H_2 \rightarrow 2NH_3$  is carried out. The standard free energy of formation of  $NH_3$  is -16.4 kJ/mol. The partial pressures of  $N_2$ ,  $H_2$  and  $NH_3$  become 50 bar, 2 bar and 200 bar, respectively after one hour of mixing. What will be free energy at this stage of the reaction?
  - A.  $+5.02 \text{ kJ mol}^{-1}$
- B.  $-5.02 \text{ kJ mol}^{-1}$
- C.  $-27.88 \text{ kJ mol}^{-1}$
- D.  $+27.88 \text{ kJ mol}^{-1}$
- 2. Select the mixture that will have the lowest pH at 298 K?
  - A.  $10 \text{ mL } 0.05 \text{ N CH}_3\text{COOH} + 5 \text{ mL } 0.1 \text{ N}$

 $NH_4OH$ 

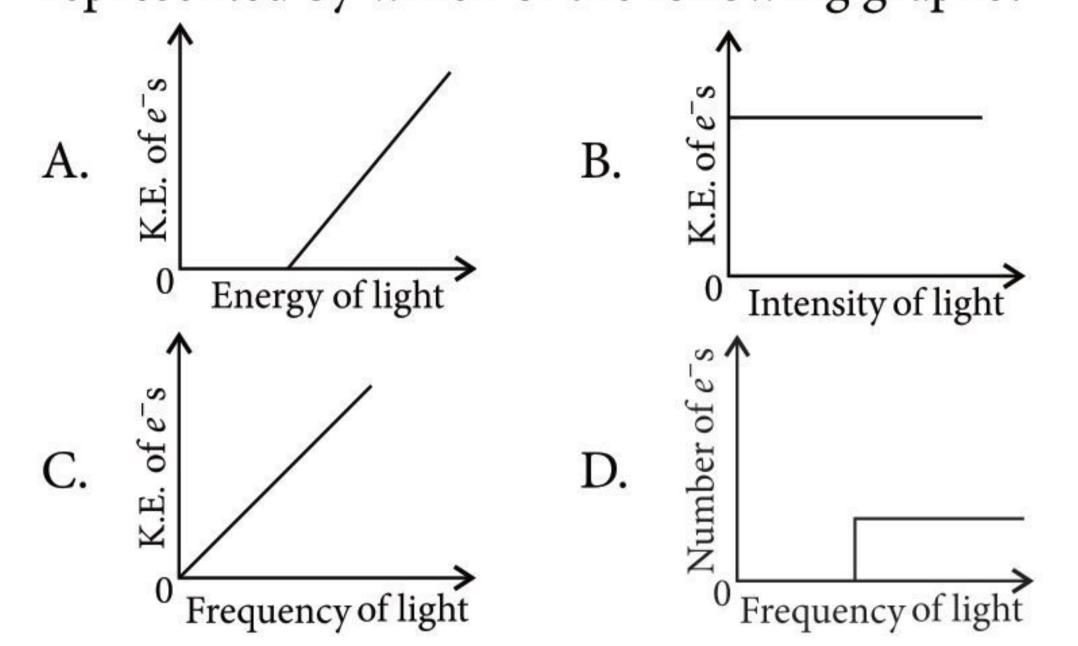
- B.  $5 \text{ mL } 0.2 \text{ N NH}_4\text{Cl} + 5 \text{ mL } 0.2 \text{ N NH}_4\text{OH}$
- C.  $5 \text{ mL } 0.1 \text{ N CH}_3\text{COOH} +$

10 mL 0.05 N CH<sub>3</sub>COONa

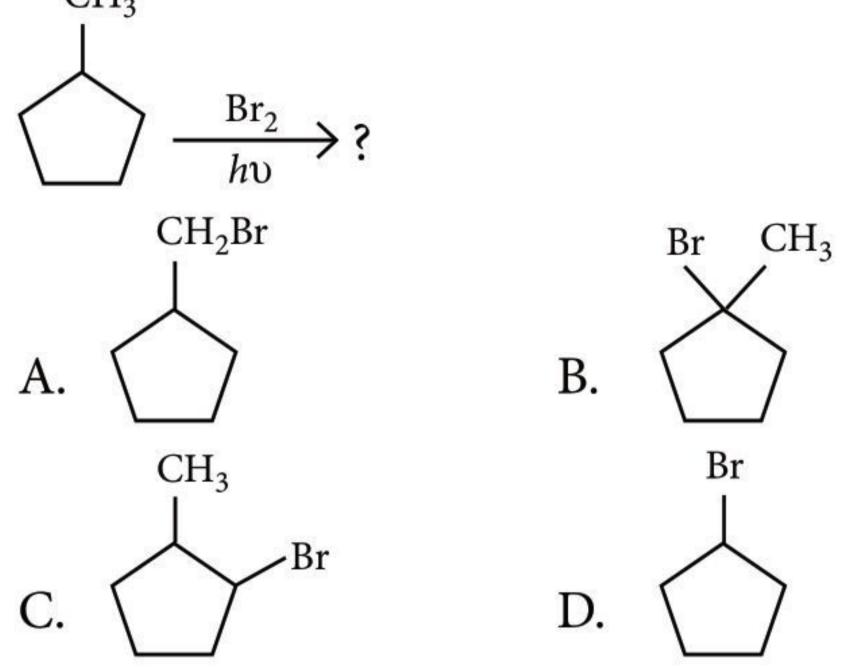
- D. 5 mL 0.1 N CH<sub>3</sub>COOH + 5 mL 0.1 N NaOH
- 3. Consider the following balanced chemical reaction,  $IO_3^- + aI^- + bH^+ \rightarrow cH_2O + dI_2$  a, b, c and d respectively can be assigned as
  - A. 5, 6, 3, 3
- B. 5, 3, 6, 3
- C. 3, 5, 3, 6
- D. 5, 6, 5, 5
- 4. Mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of a substance will (considering  $\frac{1}{6}$  in place of  $\frac{1}{12}$ )

- A. decrease to half
- B. increase two fold
- C. remain unchanged
- D. be a function of the molecular mass of the substance.
- 5. The correct order of ionic radii is
  - A.  $N^{3-} > O^{2-} > F^{-} > Na^{+}$
  - B.  $N^{3-} > Na^+ > O^{2-} > F^-$
  - C.  $Na^+ > O^{2-} > N^{3-} > F^-$
  - D.  $O^{2-} > F^- > Na^+ > N^{3-}$
- 6. Consider the following statements and select the incorrect one.
  - A. Hybridisation is the mixing of atomic orbitals and their simultaneous combination into molecular orbitals.
  - B.  $sp^2$  hybrid orbitals are formed from two p-atomic orbitals and one s-atomic orbital.
  - C.  $dsp^2$  hybrid orbitals are all at 90° to one another.
  - D.  $d^2sp^3$  hybrid orbitals are directed towards the corners of a regular octahedron.
- 7. An allyl isocyanide has
  - A.  $9 \sigma$  and  $4 \pi$  bonds
  - B.  $8 \sigma$  and  $5 \pi$  bonds
  - C. 9  $\sigma$ , 3  $\pi$  and 2 non-bonded electrons
  - D.  $8 \sigma$ ,  $3 \pi$  and 4 non-bonded electrons.

The relationship between incident light and the electron ejected from metal surface is not represented by which of the following graphs?



The major product formed in following reaction is  $CH_3$ 



10. Select the correct order of basicity from weak to strong for the following intermediates.

(i) 
$$H_3C - C^-$$
 (ii)  $H_2C = CH - CH_2$   $CH_3$ 

(iv) 
$$\bar{C}H_3$$

(v) 
$$\bar{C}N$$

A. 
$$(v) < (iii) < (ii) < (iv) < (i)$$

B. 
$$(iii) < (i) < (ii) < (iv) < (v)$$

C. 
$$(v) < (i) < (iv) < (ii) < (iii)$$

D. 
$$(iii) < (iv) < (ii) < (i) < (v)$$

11. Match column I with column II and select the correct option.

	С	olum	n I		Column II
	(Mo	lecule	/Ion)		(Molecular geometry)
Ι	HgC	$l_2$		1.	Tetrahedral
II	$NH_4^+$	<u>-</u> 6		2.	Trigonal bipyramidal
III	SF <sub>6</sub>	20		3.	Linear
IV	PCl <sub>5</sub>			4.	Octahedral
	I	II	III	Ι	$\mathbf{V}$
A.	4	3	2	1	
В.	3	1	4	2	2
C.	3	2	1	4	l E

12. Which of the following equations give ionic product of water?

(i) 
$$NH_{3(aq)} + H_2O \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$$

(ii) 
$$NH_{4(aq)}^+ + H_2O \rightleftharpoons H_3O^+ + NH_{3(aq)}$$

(iii) 
$$NH_{2(aq)}^- + H_2O \rightleftharpoons NH_{3(aq)} + OH^-$$

(iv) 
$$NH_{3(aq)} + OH_{(aq)}^- \rightleftharpoons NH_{2(aq)}^- + H_2O$$

An oxide of iodine (At. mass of I = 127) contains 25.4 g of iodine and 8 g of oxygen. Its formula could be

A. 
$$I_2O_3$$

B. 
$$I_2O$$

C. 
$$I_2O_5$$

D. 
$$I_2O_9$$

14. Consider the following ionisation enthalpies of two elements 'M' and 'N':

T-14	Ionis	ation enthal	py (kJ/mol)
Element	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
M	899	1757	14847
N	737	1450	7731

Which of the following statements is correct?

- A. Both 'M' and 'N' belong to group-2 where 'M' comes below 'N'.
- Both 'M' and 'N' belong to group-2 where 'N' comes below 'M'.
- Both 'M' and 'N' belong to group-1 where 'N' comes below 'M'.
- Both 'M' and 'N' belong to group-1 where 'M' comes below 'N'.
- 15. Select the correct statement.
  - A. Quantum numbers (n, l, m, s) are obtained arbitrarily.

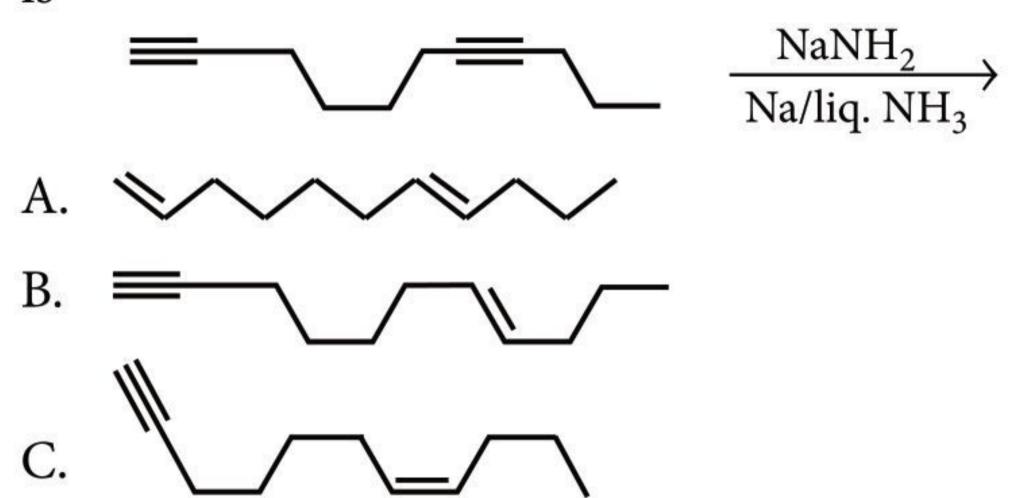


D. 2 3 4 1

- All the quantum numbers (n, l, m, s) for any pair of electrons in an atom can be identical under special circumstances.
- C. All the quantum numbers (n, l, m, s) may not be required to describe an electron of an atom completely.
- D. All the quantum numbers (n, l, m, s) are required to describe an electron of an atom completely.

#### **ACHIEVERS SECTION**

16. The major product formed in the following reaction is



17. Match Column I with Column II and select the correct option.

	Column I (Species)		Column II (Hybrid Orbitals)
P.	SF <sub>4</sub>	(i)	$sp^3d^2$
Q.	IF <sub>5</sub>	(ii)	$d^2sp^3$
R.	$NO_2^+$	(iii)	$sp^3d$
S.	$NH_4^+$	(iv)	$sp^3$
		(v)	sp

- A. P (iii), Q (i), R (v) and S (iv)
- B. P (ii), Q (i), R (iv) and S (v)
- C. P (iv), Q (iii), R (i) and S (v)
- D. P (i), Q (ii), R (v) and S (iii)
- 18. The standard state Gibbs free energies of formation of  $C_{\text{(graphite)}}$  and  $C_{\text{(diamond)}}$  at T = 298 K are  $\Delta_f G^{\circ}[C_{\text{(graphite)}}] = 0 \text{ kJ mol}^{-1};$  $\Delta_f G^{\circ}[C_{\text{(diamond)}}] = 2.9 \text{ kJ mol}^{-1}$

By standard state, it means that the pressure

should be 1 bar, and substance should be pure at a given temperature. In the conversion of graphite to diamond, the volume gets reduced by  $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . If  $C_{\text{(graphite)}}$  is converted to  $C_{\text{(diamond)}}$  isothermally at T = 298 K, the pressure at which  $C_{\text{(graphite)}}$  is in equilibrium with  $C_{\text{(diamond)}}$ , is [Useful information:  $1 J = 1 \text{ kg m}^2 \text{s}^{-2}$ ;  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{s}^{-2}$ ;  $1 \text{ bar} = 10^5 \text{ Pa}$ 

- A. 29001 bar
- 58001 bar
- 14500 bar
- 1450 bar
- 19. Solid AgNO<sub>3</sub> is gradually added to the solution having 0.1 M in  $\text{Cl}^-$  and 0.001 M in  $\text{CrO}_4^{2-}$ . Assuming there is no change in volume after addition.

[Given:  $K_{sp}(AgCl) = 1.7 \times 10^{-10} \text{ M}^2$  and  $K_{sp}(Ag_2CrO_4) = 1.9 \times 10^{-12} \text{ M}^3$ ].

Select correct statement from the following.

- A. AgCl will precipitate first as the amount of Ag<sup>+</sup> needed to precipitate is low.
- B. Ag<sub>2</sub>CrO<sub>4</sub> precipitates first because the amount of Ag<sup>+</sup> needed is low.
- C. AgCl precipitates first because its  $K_{sp}$  is high.
- D.  $Ag_2CrO_4$  precipitates first as its  $K_{sp}$  is low.
- 20. Consider the following statements regarding the interpretation of the atomic orbitals and select the correct one.
  - An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.
  - (ii) For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.
  - (iii) According to wave mechanics, the ground state angular momentum is equal to  $h/2\pi$ .
  - (iv) The plot of  $\psi$  vs r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

  - A. (i) and (iv) only B. (i) and (iii) only
  - (i) and (ii) only
- D. (ii) and (iii) only

#### Darken your choice with HB Pencil

8			Dai	Kell ye	di choice with hib i e	11011			
1.	A B C D	5.	A B C D	9.	A B C D	13.	A B C D	17.	A B C D
2.	A B C D	6.	A B C D	10.	A B C D	14.	A B C D	18.	A B C D
3.	A B C D	7.	A B C D	11.	A B C D	15.	A B C D	19.	A B C D
4.	A B C D	8.	A B C D	12.	A B C D	16.	A B C D	20.	A B C D

#### SOLUTIONS

1. (C): 
$$\Delta G = \Delta G^{\circ} + RT \ln \left[ \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} \right]$$

1. (C): 
$$\Delta G = \Delta G^{\circ} + RT \ln \left[ \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} \right]$$
 force of attra decreases. Here  $N'$  comes be  $N'$  comes by  $N'$  comes b

- 3. (A): The complete balanced equation is  $IO_3 + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$
- 4. (A): 1 atomic mass unit on the scale of 1/6 of C-12 = 2 amu on the scale of 1/12 of C-12.

Now, atomic mass of an element

= 
$$\frac{\text{Mass of one atom of the element}}{1 \text{ amu (Here on the scale of } \frac{1}{6} \text{ of C - 12)}}$$
  
=  $\frac{\text{Mass of one atom of the element}}{2 \text{ amu (Here on the scale of } \frac{1}{12} \text{ of C - 12)}}$ 

- Numerically, the mass of a substance will become half of the normal scale.
- 5. (A)
- 6. (C): In  $dsp^2$  hybrid orbitals, two adjacent orbitals are at 90° whereas opposite hybrid orbitals are at 180°.
- 7. (C):  $CH_2 = CH CH_2 N \Longrightarrow C$ There are  $9\sigma$ ,  $3\pi$  and 2 non-bonded electrons.
- 8. (C)

9. (B) : 
$$Br_2 \xrightarrow{hv} 2B\mathring{r}$$

$$CH_3$$

This will react with to give the most stable 3° free radical.

- 10. (A) : Basicity  $\infty$ Electronegativity
- 11. (B)
- Molar mass

Moles of 
$$O = \frac{8}{16} = \frac{1}{2} = 0.5 \text{ mol}$$

Ratio of I : O is 2:5. Thus, molecular formula will be  $I_2O_5$ . 14. (B): As the third ionisation energy of M and N are very high as compared to corresponding second ionisation energy, thus, there must be two electrons in their valence

shells. Hence, elements M and N belong to group-2.

On going down the group, the atomic size increases, so force of attraction between valence electron and nucleus decreases. Hence, ionisation energy decreases. Thus, 'N' comes below 'M'.

$$\frac{16. (B)}{=} \qquad Na/liq. NH_3 = \qquad \qquad$$

17. (A)

18. (C): 
$$C_{\text{(graphite)}} \longrightarrow C_{\text{(diamond)}}$$
 (Isothermally)  
 $\Delta_r G^{\circ} = \Delta G^{\circ}_{\text{(diamond)}} - \Delta G^{\circ}_{\text{(graphite)}}$   
 $= 2.9 - 0 = 2.9 \text{ kJ mol}^{-1}$ 

Gibbs free energy is the maximum useful work, then  $-\Delta G = w_{\text{max}} = P\Delta V; -2.9 \times 10^3 = -P \times 2 \times 10^{-6}$ 

$$P = \frac{2.9 \times 10^3}{2 \times 10^{-6}} = 1.45 \times 10^4 \text{ bar} = 14500 \text{ bar}$$

19. (A): (i) Concentration of Ag<sup>+</sup> required for precipitation of AgCl.

$$K_{sp}(AgCl) = [Ag^{+}][Cl^{-}]$$
  
 $1.7 \times 10^{-10} = [Ag^{+}][0.1]$   
 $[Ag^{+}] = 1.7 \times 10^{-9}M$ 

(ii) Concentration of Ag<sup>+</sup> required for precipitation of  $Ag_2CrO_4$ .

$$K_{sp}(Ag_2CrO_4) = [Ag^+]^2 [CrO_4^{2-}]$$
  
 $1.9 \times 10^{-12} = [Ag^+]^2 (0.001)$   
 $[Ag^+] = \sqrt{1.9 \times 10^{-9}} = \sqrt{19} \times 10^{-5}$ 

Amount of Ag<sup>+</sup> required to precipitate is low for Cl<sup>-</sup>. So, AgCl gets precipitated first.

20. (A)

For other sections/subjects please refer to Physics For You and Biology Today





The three letter word is E R M.

THERMOSTAT ISOTH E R M THERMOMETER GERMANIUM EXOTHER MIC

Winners: Debosmita Santra, Gagan Marer and Ananya Goswami



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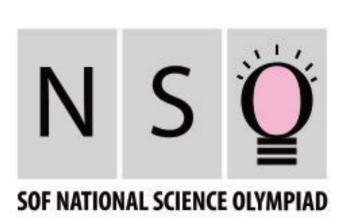


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Time . 1 hr

#### SYLLABUS\*

**Section** – **1** : *Physics* : Electricity and Magnetism, Electromagnetic Induction, Alternating current, Electromagnetic waves, Optics, Modern Physics, Semiconductor Electronics, Communication Systems.

Chemistry: Solid State, Solutions, Electrochemistry, Chemical Kinetics, Surface Chemistry, General Principles and Processes of Isolation of Elements, p-Block Elements (Group 15 to 18), d- & f-Block Elements, Coordination Compounds, Haloalkanes and Haloarenes, Alcohols, Phenols and Ethers, Aldehydes, Ketones and Carboxylic Acids, Amines, Biomolecules, Polymers, Chemistry in Everyday Life.

**Section** – **2**: Higher Order Thinking Questions - Syllabus as per Section – 1. Section – 3: Relations and Functions, Inverse Trigonometric Functions, Matrices and Determinants, Continuity and Differentiability, Application of Derivatives,

Integrals, Application of Integrals, Differential Equations, Vector Algebra, Three Dimensional Geometry, Probability, Linear Programming.

OR

Section – 3: Reproduction, Genetics and Evolution, Biology in Human Welfare, Biotechnology, Ecology.

#### **Practice Questions**

1. The mathematical relation between degree of dissociation ( $\alpha$ ) of a weak electrolyte,  $A_x B_v$  and van't Hoff factor (i) is

A. 
$$\alpha = \frac{i-1}{(x+y-1)}$$

A. 
$$\alpha = \frac{i-1}{(x+y-1)}$$
 B.  $\alpha = \frac{i-1}{(x+y+1)}$ 

C. 
$$\alpha = \frac{(x+y-1)^{i-1}}{i-1}$$

C. 
$$\alpha = \frac{(x+y-1)}{i-1}$$
 D.  $\alpha = \frac{(x+y+1)}{i-1}$ 

Consider the following sequence of reactions:

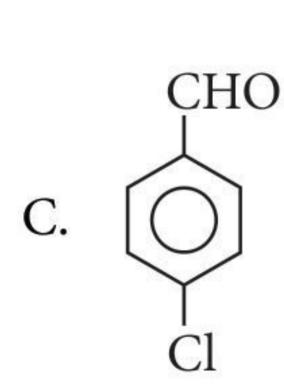
$$(P) \xrightarrow{\text{(i) Br}_2/\text{Fe}} (Q) \xrightarrow{\text{CH}_2 = O} (R) \xrightarrow{\text{Cl}_2/\text{Fe}} (S)$$

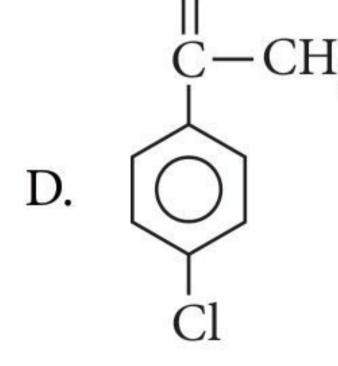
$$(P) \xrightarrow{\text{(ii) Mg/ether}} (Q) \xrightarrow{\text{CH}_2 = O} (R) \xrightarrow{\text{Cl}_2/\text{Fe}} (S)$$

$$(P) \xrightarrow{\text{(iii) Mg/ether}} (Q) \xrightarrow{\text{CH}_2 = O} (R) \xrightarrow{\text{Cl}_2/\text{Fe}} (S)$$

Identify the final product T.

A. 
$$CH_2OH$$





Total Questions : 50

**CLASS XII** 

Total Questions: 50			nme : i ni.
	PATTERN & MAI	RKING SCHEME	
Section	(1) Physics & Chemistry	(2) Achievers Section	(3) Mathematics or Biology
No. of Questions	25	5	20
Marks per Ques.	1	3	1

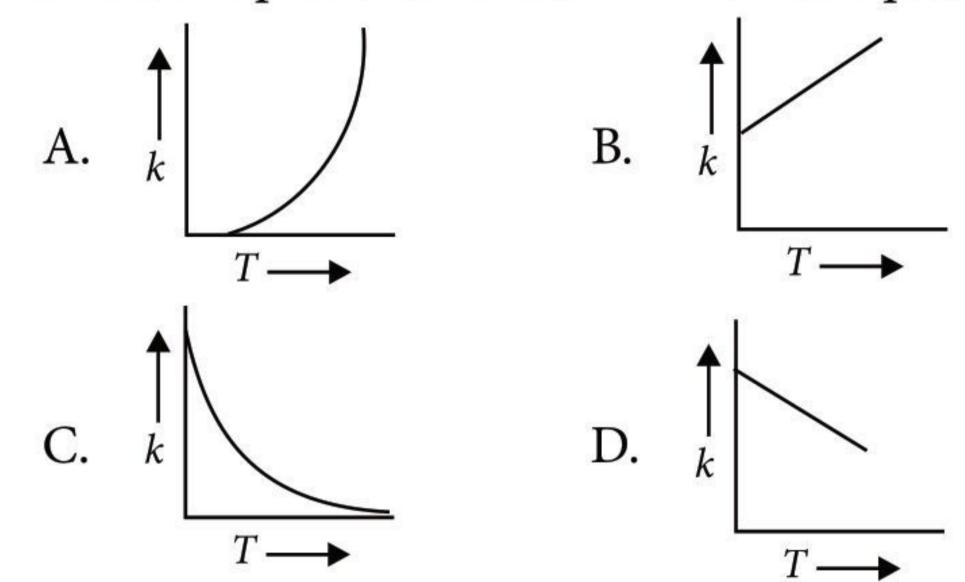
The ion which has zero CFSE in octahedral field is

A.  $Cr^{3+}$  (high spin) B.  $Co^{2+}$  (low spin) C.  $Fe^{3+}$  (low spin) C.  $Fe^{3+}$  (high spin).

4. Select the correct set of stereochemical relationship amongst the following monosaccharides.

- (I) and (III) are epimers; (II) and (IV) are anomers.
- (I) and (II) are epimers; (III) and (IV) are В. anomers.
- (I) and (III) are anomers; (I) and (II) are epimers.

- (I) and (II) are anomers; (III) and (IV) are epimers.
- Various plots showing the variation of the rate constant (k) with temperature (T) are shown below. Select the plot that follows Arrhenius equation.



- In nitroprusside ion, the iron and NO exist as Fe<sup>II</sup> and NO<sup>+</sup> rather than Fe<sup>III</sup> and NO. These forms can be differentiated by
  - estimating the concentration of iron
  - measuring the concentration of CN
  - measuring the solid state magnetic moment
  - thermally decomposing the compound.

The yield of this reaction is

- 100%B. 10%
- D. 0%

50%

Which one of the following chlorohydrocarbon readily undergoes solvolysis?

A. 
$$\langle \bigcirc \rangle$$
—CH<sub>2</sub>Cl C.  $\langle \bigcirc \rangle$ —CH<sub>2</sub>CH<sub>2</sub>Cl C. CH<sub>2</sub>CH<sub>2</sub>Cl D.  $\langle \bigcirc \rangle$ —Cl

Consider the following reactions,

and select the correct option.

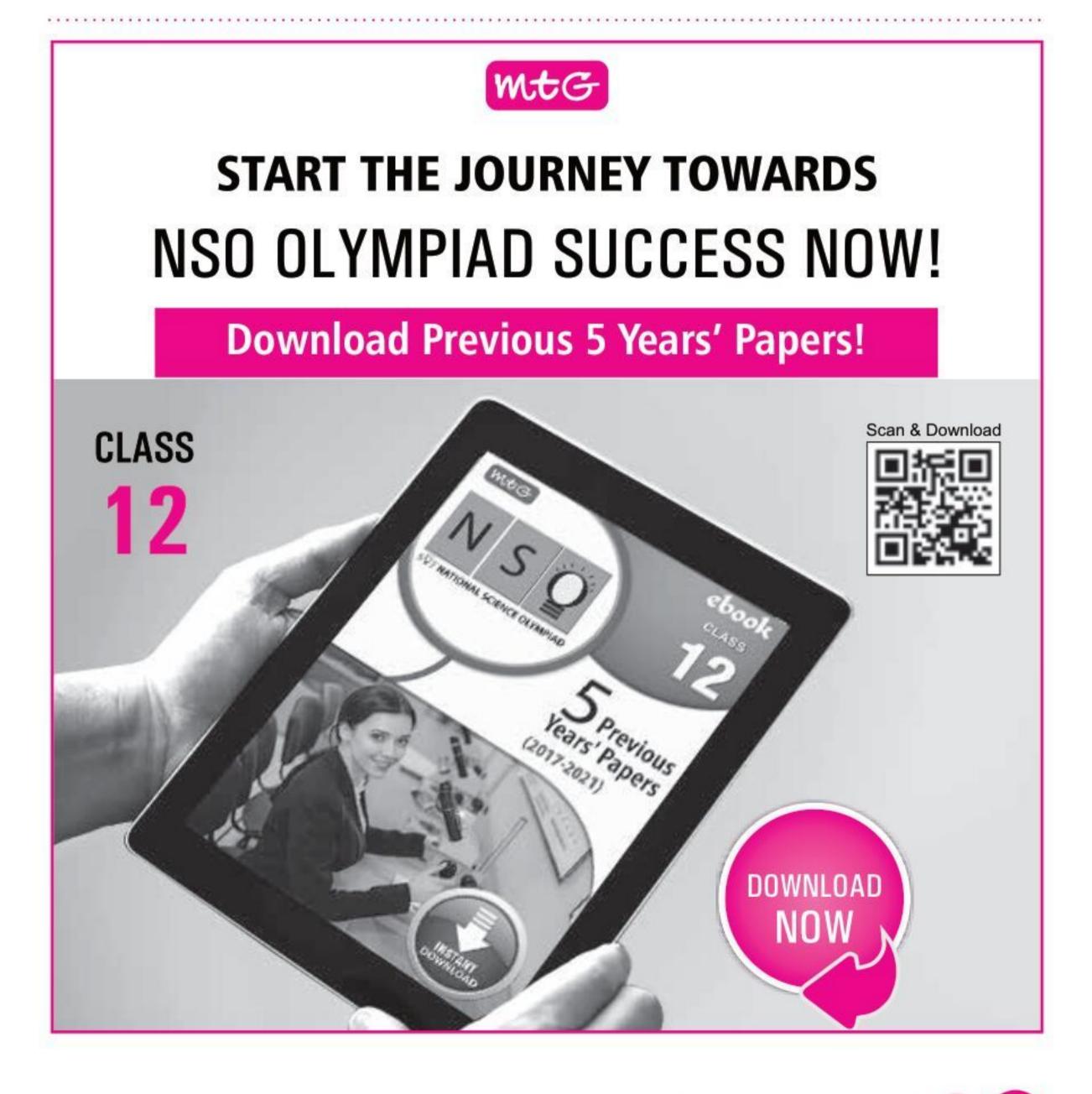
- A. M and N both are 3-methoxy-2-methyl -2-butanol.
- M and N both are 3-methoxy-3-methyl-2butanol.
- *M* is 3-methoxy-3-methyl-2-butanol and *N* is 3-methoxy-2-methyl-2-butanol.
- *M* is 3-methoxy-2-methyl-2-butanol and *N* is 3-methoxy-3-methyl-2-butanol.
- 10. Anhydrous ferric chloride can be prepared by
  - A. heating hydrated ferric chloride at a high temperature in a stream of air

- heating metallic iron in a stream of dry chlorine gas
- reaction of metallic iron with concentrated hydrochloric acid
- reaction of metallic iron with dilute nitric acid.
- 11. During depression of freezing point in a solution, which of the following are in equilibrium?
  - A. liquid solvent, solid solvent
  - liquid solvent, solid solute
  - liquid solute, solid solute
  - solid solute, solid solvent.
- 12. An electric current is passed through an aqueous solution of a mixture of alanine (isoelectric point 6.0), glutamic acid (3.2) and arginine (10.7) buffered at pH 6. What will the fate of the three acids?
  - All these remain uniformly distributed in solution.
  - Glutamic acid migrates to anode at pH 6. Arginine present as a cation and migrates to the cathode. Alanine as a dipolar ion remains uniformly distributed in solution.
  - Glutamic acid will migrate to cathode while others remain uniformly distributed in solution.
  - All three move to anode.
- 13. In the following sequence of reactions:

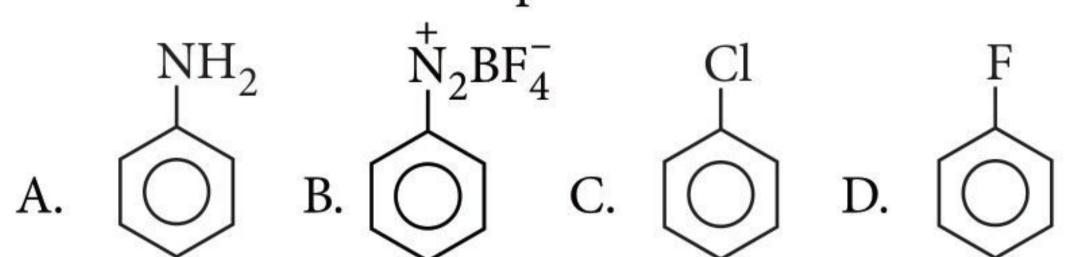
$$+ HOCl \xrightarrow{H^+} W \xrightarrow{\text{liq. NH}_3} X \xrightarrow{\text{HBF}_4} Y$$

$$X \xrightarrow{\text{NaNH}_2/} X$$

$$X \xrightarrow{\text{NaNO}_2} X$$



What will be the final product Z.



- (unit Siemen, S) 14. Conductivity proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel. What will be the unit of the constant of proportionality?

  - A.  $S \text{ m mol}^{-1}$  B.  $S \text{ m}^2 \text{ mol}^{-1}$
  - C.  $S^{-2}m^2$  mol
- D.  $S^2 \text{ m}^2 \text{ mol}^{-2}$
- 15. Saturated solution of KNO<sub>3</sub> is used to make 'salt-bridge' because
  - A. velocity of  $K^+$  is larger than that of  $NO_3^-$
  - velocity of NO<sub>3</sub><sup>-</sup> is smaller than that of K<sup>+</sup>
  - velocities of both K<sup>+</sup> and NO<sub>3</sub> are nearly the same
  - KNO<sub>3</sub> is highly soluble in water.

#### **ACHIEVERS SECTION**

16. The major product of the following reaction sequence is

- 17. The correct order of intensity of colours of the compounds is
  - $[Ni(H_2O)_6]^{2+} > [NiCl_4]^{2-} > [Ni(CN)_4]^{2-}$
  - $[NiCl_4]^{2-} > [Ni(CN)_4]^{2-} > [Ni(H_2O)_6]^{2+}$
  - $[NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+} > [Ni(CN)_4]^{2-}$
  - $[Ni(CN)_4]^{2-} > [NiCl_4]^{2-} > [Ni(H_2O)_6]^{2+}$

18. The products formed during the following reaction are

$$CH_{3} \xrightarrow{|CH_{3}|} CH_{3} - CH_{3} - CH_{3} + HI \xrightarrow{373 \text{ K}} ?$$

$$CH_{3} \xrightarrow{|CH_{3}|} CH_{3}$$

A. 
$$CH_{3}OH + CH_{3} - C - I$$
 $CH_{3}$ 
 $CH_{3}$ 
 $CH_{3}$ 

B. 
$$CH_4 + H_3C - C - OI$$
 $CH_3$ 
 $CH_4 + C - C - OI$ 
 $CH_3$ 

C. 
$$CH_{3}I + CH_{3} - C - OH$$
 $CH_{3}I + CH_{3} - C - OH$ 
 $CH_{3}I + CH_{3} - C - OH$ 

D. 
$$CH_3OI + H_3C - C - H$$
  
 $CH_3$   
 $CH_3$ 

- 19. The correct statements about Cr<sup>2+</sup> and Mn<sup>3+</sup> are [Atomic numbers of Cr = 24 and Mn = 25]
  - $Cr^{2+}$  is a reducing agent.
  - Mn<sup>3+</sup> is an oxidizing agent.
  - III. Both  $Cr^{2+}$  and  $Mn^{3+}$  exhibit  $d^4$  electronic configuration.
  - IV. When Cr<sup>2+</sup> is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration.
  - A. I, II and III only
- B. III and IV only
- I, II and IV only
- D. II and IV only
- 20. For a first order reaction, select the correct statements.
  - The degree of dissociation is equal to  $(1 e^{-kt})$ .
  - A plot of reciprocal of concentration of the reactant vs time gives a straight line.
  - III. The time taken for the completion of 75% reaction is thrice the  $t_{1/2}$  of the reaction.
  - The pre-exponential factor in the Arrhenius equation has the dimension of time,  $T^{-1}$ .
  - I and IV only
- B. II and III only
- I and III only
- D. II and IV only

#### Darken your choice with HB Penci

				out Ken	your enoice with 11b I enc				
1.	A B C D	5.	A B C D	9.	A B C D	13.	A B C D	17.	A B C D
2.	A B C D	6.	A B C D	10.	A B C D	14.	A B C D	18.	A B C D
3.	A B C D	7.	A B C D	11.	A B C D	15.	A B C D	19.	A B C D
4.	A B C D	8.	A B C D	12.	A B C D	16.	A B C D	20.	A B C D

#### SOLUTIONS

1. (A): 
$$A_x B_y \rightarrow x A^{y+} + y B^{x-}$$
  
initial moles 1 0 0  
final moles  $1 - \alpha = x\alpha = y\alpha$   

$$i = \frac{1 - \alpha + x\alpha + y\alpha}{1} = 1 + \alpha(x + y - 1)$$

$$\therefore \alpha = \frac{i - 1}{(x + y - 1)}$$

2. (C): 
$$\underbrace{ (i) \text{ Br}_2/\text{Fe} }_{\text{(ii) Mg/ether}} \underbrace{ (i) \text{ Br}_2/\text{Fe} }_{\text{(ii) Mg/ether}} \underbrace{ (Q) }_{\text{(Q)}} \underbrace{ (R) }_{\text{(R)}}$$

$$\underbrace{ (CH_2 \text{CH}_2 \text{CH$$

*p*-Chlorobenzaldehyde

3. (D): 
$$Cr^{3+}$$
 (high spin)  $\Rightarrow t_{2g}^{3}e_{g}^{0}$ ;  $CFSE = -0.4 \times 3 = -1.2 \Delta_{o}$   $Co^{2+}$  (low spin)  $\Rightarrow t_{2g}^{6}e_{g}^{1}$ ;  $CFSE = -0.4 \times 6 + 0.6 \times 1 = -1.8 \Delta_{o}$   $Fe^{3+}$  (low spin)  $\Rightarrow t_{2g}^{5}e_{g}^{0}$ ;  $CFSE = -0.4 \times 5 = -2.00 \Delta_{o}$   $Fe^{3+}$  (high spin)  $\Rightarrow t_{2g}^{3}e_{g}^{2}$ ;  $CFSE = -0.4 \times 3 + 0.6 \times 2 = 0.0 \Delta_{o}$ 

4. (C): (I) and (III) differ in configuration at C<sub>1</sub> and hence are anomers while (I) and (II) differ in configuration at  $C_4$  and hence are epimers.

5. (A)

(C): Magnetic moment μ is given by  $\mu = \sqrt{n(n+2)}$  B.M.

Where, *n* is the number of unpaired electrons. Number of unpaired electrons in various species are Fe<sup>2+</sup>: It is  $3d^6$  *i.e.* 4 unpaired electrons Fe<sup>3+</sup>: It is  $3d^5$  *i.e.* 5 unpaired electrons

\*NO or  $^{\dagger}N = \ddot{O}$ ; in this all the electrons are paired.

NO or  $X \cong O$ , we have a three electron bond so it has an odd (unpaired electron). *i.e.* n = 1Since, they (i.e. +NO and NO) have different number of unpaired electrons so they can be differentiated by the measurement of the solid state magnetic moment 21. (a,b) 22. (a,b,c) 23. (a,d) 24. (144) 25. (3.42) of nitroprusside ion.

7. (D): NaBH<sub>4</sub> cannot reduce carbon-carbon double bond which is conjugated with carbon-oxygen double bond.

8. (A) 9. (D)

10. (B): 
$$2Fe+3Cl_2 \longrightarrow 2FeCl_3$$
 (Dry) (Anhydrous)

11. (A)

12. (B): At pH = 6, glutamic acid exists as a dianionic species and migrates to anode while arginine exists as cationic species and moves to cathode. Alanine does not migrate to any electrode at its isoelectric point.

13. (D): At first, generation of electrophile (chloronium ion, Cl<sup>+</sup>) takes place which attacks on benzene.

$$C_6H_6 + Cl^+ \xrightarrow{-H^+} C_6H_5Cl$$
Benzene Chlorobenzene (W)

A on treatment with NaNH<sub>2</sub>/liq. NH<sub>3</sub> gives aniline (B).

Cl NaNH<sub>2</sub>/liq. NH<sub>3</sub> 
$$\longrightarrow$$
 NH<sub>3</sub> Addition NH<sub>2</sub>

NaNO<sub>2</sub>  $\longrightarrow$  NH<sup>+</sup><sub>3</sub>BF<sup>-</sup><sub>4</sub>  $\longrightarrow$  HBF<sub>4</sub>

Anilinium tetrafluoroborate

$$\begin{bmatrix} \uparrow \\ NBF_{4} \end{bmatrix} \xrightarrow{(Y)} \begin{bmatrix} (Y) \\ -N_{2}, -BF_{3} \\ \Delta \end{bmatrix} \xrightarrow{Fluorobenzene} F$$

14. (B): According to the given information.

Area × Concentration Conductivity ∞ length of vessel

Conductivity = 
$$K \times \frac{\text{Area} \times \text{Concentration}}{\text{length of vessel}}$$

Unit of constant, 
$$K = \frac{\text{S. m}}{\text{m}^2 \times \text{mol m}^{-3}} = \text{S m}^2 \text{ mol}^{-1}$$

15. (C)

#### MONTHLY TEST DRIVE CLASS XII ANSWER (c) **2.** (b) **3.** (c) **5**. (a) 7. (c) 8. (b) 9. (c) 10. (b) (a) **11.** (b) **12.** (d) **13.** (a) **14.** (a) **15.** (c) **18.** (a) **16.** (c) **17.** (d) **20**. (c,d) **28**. (c) **29**. (b) **30**. (b) **26**. (4) **27**. (b)

16. (B) : 
$$C = CH_3$$
  $C = CH_3$   $C = CH_3$ 

17. (C)

18. (A):

19. (A): (I)  $Cr^{2+}$  is a reducing agent, it gets oxidised to  $Cr^{3+}$  (3 $d^3$  or  $t_{2g}^3$ , stable half-filled configuration).

(II)  $Mn^{3+}$  is an oxidizing agent, it gets reduced to  $Mn^{2+}$  (3 $d^5$ , most stable, half-filled configuration).

(III) Cr (24) :  $3d^44s^2$ ; Mn (25) :  $3d^54s^2$ Cr<sup>2+</sup> :  $3d^4$   $Mn^{3+}:3d^4$ 

HCHO/H+

(Acetal formation takes place)

Both  $Cr^{2+}$  and  $Mn^{3+}$  exhibit  $d^4$  electronic configuration. (IV) When  $Cr^{2+}$  is used as a reducing agent, the chromium ion attains  $d^3$  electronic configuration.

**20.** (A): For a first order reaction,  $\alpha$  is the degree of dissociation

$$\therefore k \cdot t = \ln \frac{1}{1 - \alpha} = -\ln (1 - \alpha)$$
or  $e^{-k.t.} = (1 - \alpha)$  or  $\alpha = 1 - e^{-k.t}$ 
As, Arrhenius equation is,  $k = A.e^{(-E_a/RT)}$ 

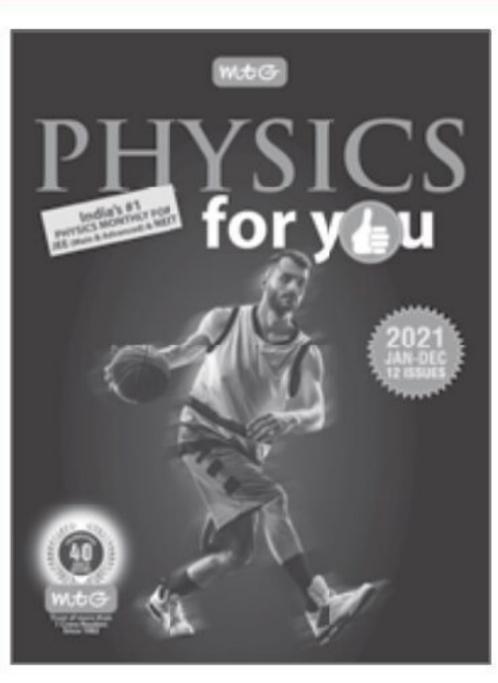
The dimensions of pre-exponential factor (A) are the same as those of k, which is  $T^{-1}$  for a first order reaction.

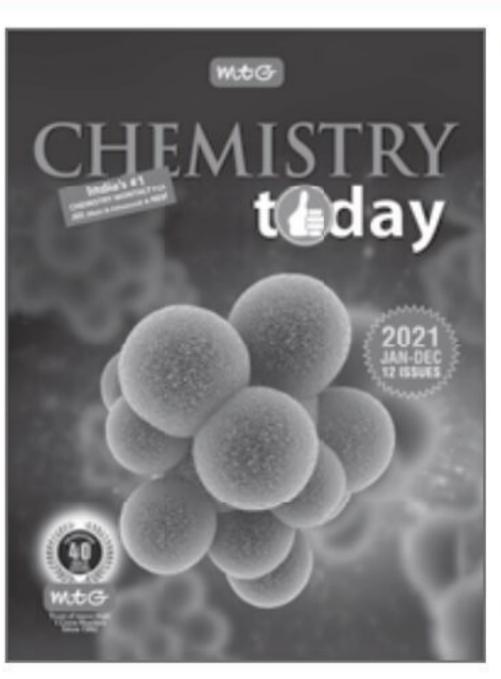
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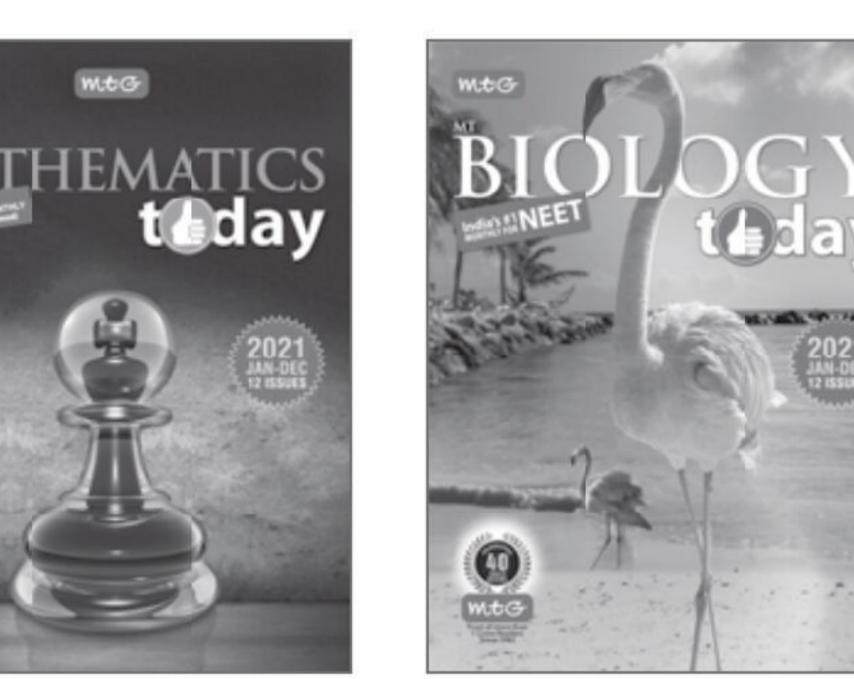


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- Few general names are given along with their 5.  $sp^3d^2$  hybridization is observed in valence shell configurations. Mark the incorrect name.
  - (a)  $ns^2 np^6$  Noble gases
  - (b)  $ns^2 np^5$  Halogens
  - (c)  $ns^1$  Alkali metals
  - (d)  $ns^2 np^2$  Chalcogens
- The balancing of chemical equations is based upon the law of
  - (a) combining volumes
  - (b) multiple proportions
  - conservation of mass
  - (d) definite proportions.
- If the four tubes of a car are filled to the same pressure with  $N_2$ ,  $O_2$ ,  $H_2$  and He separately, then which one will be filled first?
  - (a)  $N_2$
- (b)  $O_2$
- (c)  $H_2$
- The nineteenth electron of chromium has which of the following set of quantum numbers?
  - n (a) 3
  - (b) 3
  - (c) 4 0 0 + 1/2
  - (d) 4

- - (a)  $BrF_3$  (b)  $ClF_3$  (c)  $BrCl_3$  (d)  $ICl_5$

- Which of the following does not result an increase in the entropy?
  - (a) Crystallisation of sucrose from solution
  - (b) Rusting of iron
  - (c) Conversion of ice to water
  - (d) Vaporisation of camphor
- In a system  $A_{(s)} \rightleftharpoons B_{(g)} + 2C_{(g)}$ , doubling the equilibrium concentration of B will cause the equilibrium concentration of C to change to
  - (a) two times its original value
  - (b) one half of its original value
  - (c)  $\frac{1}{\sqrt{2}}$  times the original value
  - (d)  $\sqrt{2}$  times the original value.
- KO<sub>2</sub> (potassium superoxide) is used in oxygen cylinders in space and submarines because it
  - (a) absorbs CO<sub>2</sub> and increases O<sub>2</sub> content
  - (b) eliminates moisture
  - (c) absorbs O<sub>2</sub>
  - (d) produces ozone.
- 9. Covalency of B in  $BF_4$  is
  - (a) 5
- (b) 4 (c) 3 (d) 2

- 10. Elements of group 14 exhibit oxidation state of

  - (a) +4 only (b) +2 and +4 only
  - (c) +1 and +3 only (d) +2 only.
- 11. Kjeldahl method for estimation of nitrogen is not applicable to
  - (a) pyridine
  - (b) hexamethylene diamine
  - (c) propan-1-amine
  - (d) 2-phenylethanamine.
- 12. The IUPAC name of

- (a) 1-hydroxy-4-methylpentan-3-one
- (b) 2-methyl-5-hydroxypentan-3-one
- (c) 4-methyl-3-oxopentan-1-ol
- (d) hexan-1-ol-3-one.
- 13.  $CH \equiv CH \xrightarrow{O_3} X \xrightarrow{Zn/CH_3COOH} Y$

The compound *Y* is

- (a) CH<sub>2</sub>OHCH<sub>2</sub>OH
- (b) CH<sub>3</sub>COOH
- (c)  $C_2H_5OH$
- (d)  $CH_3CH_3$
- 14. Acid rains are produced by
  - (a) excess NO<sub>2</sub> and SO<sub>2</sub> from burning fossil fuels
  - (b) excess production of NH<sub>3</sub> by industry and coal gas
  - (c) excess release of carbon monoxide by incomplete combustion
  - (d) excess formation of CO<sub>2</sub> by combustion and animal respiration.
- 15. Which of the following statements is correct if the intermolecular forces in liquids A, B and C are in the order A < B < C?
  - (a) B evaporates more readily than A.
  - (b) *B* evaporates less readily than *C*.
  - (c) A and B evaporate at the same rate.
  - (d) A evaporates more readily than C.

#### SOLUTIONS

- 1. (d):  $ns^2np^2$  are members of carbon family. Chalcogens is the general name of group 16 elements.
- (c): Mass on both sides of the reaction equation should be conserved i.e., no change is observed in the total mass of the substances involved in a chemical reaction.

(c): We know that, PM = dRT

i.e., at constant temperature,  $P \propto \frac{1}{N}$ 

For the same pressure, the gas which has minimum molecular weight will be filled first. H<sub>2</sub> gas has minimum molecular weight among all, so H2 will be filled first.

- (c):  ${}_{24}\text{Cr} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ Nineteenth electron is  $4s^1$ . For which n = 4, l = 0, m = 0,  $s = \pm 1/2$
- 5. (d): ICl<sub>5</sub>:

Total no. of hybridised orbitals  $(H) = \frac{1}{2}(7+5) = 6$  $\Rightarrow sp^3d^2$ 

- (a): Crystallisation involves arrangement of molecules in a perfectly ordered manner i.e., minimum randomness.
- 7. (c):  $K_{eq} = [B] [C]^2$  $K_{ea} = [B_1] [C_1]^2 \qquad \text{(Initially)}$  $K_{eq} = [2B_1] [C_2]^2$  (Finally) As  $K_{eq}$  is always constant,  $[B_1] [C_1]^2 = [2B_1] [C_2]^2$

$$[C_2]^2 = \frac{[C_1]^2}{2}$$
;  $[C_2] = \frac{1}{\sqrt{2}}[C_1]$ 

- (a):  $4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$
- (b): Covalency of B in BF<sub>4</sub> ion is 4, which is also its maximum covalency.
- 10. (b): Outer electronic configuration of group-14 elements is  $ns^2np^2$ .

Thus, they can exhibit +2 oxidation state by losing 2 p-electrons or +4 oxidation state by losing all 4 valence electrons.

- 11. (a)
- $CH_3 O$  5 4 3 2 112. (a):  $CH_3 CH C CH_2 CH_2 OH$ 1-Hydroxy-4-methylpentan-3-one
- 13. (a):

$$CH \equiv CH \xrightarrow{O_3} CH \xrightarrow{CH} CH \xrightarrow{Zn/CH_3COOH} CH_2 - CH_2$$

$$O \longrightarrow O$$

$$OH OH$$

- 14. (a): Acid rains are produced by excess NO<sub>2</sub> and SO<sub>2</sub> from burning fossil fuels.
- 15. (d): Weaker the intermolecular forces, more readily the evaporation will take place.



Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 4

#### Equilibrium

- Equilibrium can be established for both physical processes and chemical reactions.
- At equilibrium, two opposing processes (forward and reverse) take place at equal rates and hence, it is called **dynamic equilibrium**.

#### PHYSICAL EQUILIBRIUM

- Involves physical changes only; includes phase transformation: Solid ⇌ Liquid; Liquid ⇌ Gas; Solid ⇌ Gas.
- Gas ⇒ Saturated solution of gas in liquid.
- Boiling point : Temperature at which Liquid 

   Gas,
   at 1 atm pressure.

#### **Reversible Reactions**

- A reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.
- Ultimately a stage comes in a reversible reaction, where concentration of both reactant and product becomes equal, which is said to be equilibrium.

#### **Irreversible Reactions**

 These are the reactions in which products do not react back to give reactants.

#### LAW OF CHEMICAL EQUILIBRIUM

• Law of chemical equilibrium is a result obtained by applying the law of mass action to a reversible reaction in equilibrium. • For example, consider a general reversible reaction,  $aA + bB \Longrightarrow cC + dD$ 

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
; where,  $K_c$  is equilibrium constant.

 $K_c$  is specific for a reaction and this equation is known as law of chemical equilibrium.

#### Equilibrium constant of a chemical reaction

When the equation is	<b>Equilibrium constant</b>
reversed	1/ <i>K</i>
divided by 2	$\sqrt{K}$
multiplied by 2	$K^2$
divided into 2 steps	$K = K_1 \times K_2$

• For a gas phase reaction,  $aA + bB \Longrightarrow cC + dD$ 

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$
 and  $K_p = K_c (RT)^{\Delta n_g}$ ;

where,  $\Delta n = (n_{\text{gaseous products}} - n_{\text{gaseous reactants}})$ 

- If  $\Delta n_g = 0$ ,  $K_p = K_c$
- If  $\Delta n_g = +\text{ve } (i.e., n_p > n_r), K_p > K_c$
- If  $\Delta n_g = -\text{ve } (i.e., n_p < n_r), K_p < K_c$

#### **Types of Chemical Equilibrium**

 Homogeneous equilibrium : All the reactants and products are in the same phase.

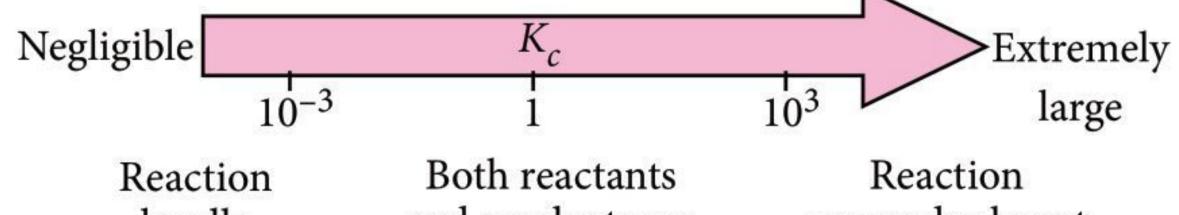
$$N_{2(g)} + 3H_{2(g)} \Longrightarrow 2NH_{3(g)}$$

 Heterogeneous equilibrium: Reactants and products are in two or more different phases.

$$C_{(g)} + H_2O_{(g)} \Longrightarrow CO_{(g)} + H_{2(g)}$$

#### APPLICATIONS OF EQUILIBRIUM CONSTANT

#### Dependence of Extent of reaction on $K_c$



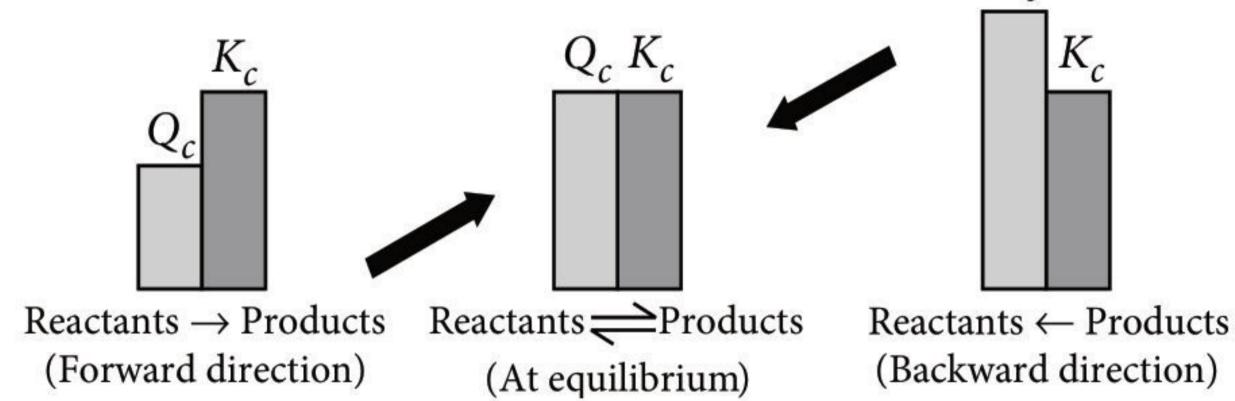
hardly and products are proceeds almost proceeds. present at equilibrium. to completion.

If the reaction is not at equilibrium then reac

• If the reaction is not at equilibrium then reaction quotient  $Q_c$  is used instead of equilibrium constant  $K_c$ .

Thus, 
$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

#### **Predicting the Reaction**



### Relation between Gibbs Free Energy and Equilibrium Constant

At equilibrium,  $\Delta G^{\circ} = -RT \ln K$ ;  $K = e^{-\Delta G^{\circ}/RT}$ 

- If  $\Delta G^{\circ}$  < 0, then K > 1 [Forward reaction is favoured.]
- If  $\Delta G^{\circ} > 0$ , then K < 1 [Reverse reaction is favoured.]
- If  $\Delta G^{\circ} = 0$ , then K = 1 [Reaction is at equilibrium.]

#### LE CHATELIER'S PRINCIPLE

• If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed.

#### **Effect of Temperature on Equilibrium Constant**

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^{\circ}}{RT^2}; \log \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

- If  $\Delta H = 0$ , *i.e.*, no heat is evolved or absorbed in the reaction,  $\log (K_2/K_1) = 0$ , or  $K_2/K_1 = 1$  or  $K_2 = K_1$  *i.e.*, equilibrium constant does not change with temperature.
- If  $\Delta H = +$ ve, *i.e.*, heat is absorbed in the reaction, then  $\log (K_2/K_1) = +$ ve or  $\log K_2 > \log K_1$  or  $K_2 > K_1$  *i.e.*, equilibrium constant increases with increase in temperature.
- If  $\Delta H = -\text{ve}$ , *i.e.*, heat is evolved in the reaction,  $\log (K_2/K_1) = -\text{ve}$  or  $\log K_2 < \log K_1$  or  $K_2 < K_1$  *i.e.*, equilibrium constant decreases with increase in temperature.

#### IONIC EQUILIBRIUM

- Substances that conduct electricity in their aqueous solutions or in molten state are called **electrolytes**.
- Strong electrolytes are completely ionised in aqueous solutions and weak electrolytes are partially ionised in aqueous solutions.
- In weak electrolytes, an equilibrium is established between ions and unionised molecules, leading to an ionic equilibrium in the aqueous solution. All acids, bases and salts may be classified as weak or strong electrolytes.
- Degree of dissociation ( $\alpha$ ) =  $\frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}$ For strong electrolytes,  $\alpha = 1$  and for weak electrolytes,  $\alpha < 1$ .
- Ostwald's dilution law: For a binary electrolyte AB.

$$AB \iff A^{+} + B^{-}$$
Initial concentration  $C = 0$  0
Conc. at equilibrium  $C(1-\alpha)$   $C\alpha$   $C\alpha$ 

where,  $\alpha$  is degree of dissociation.

$$K_a = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

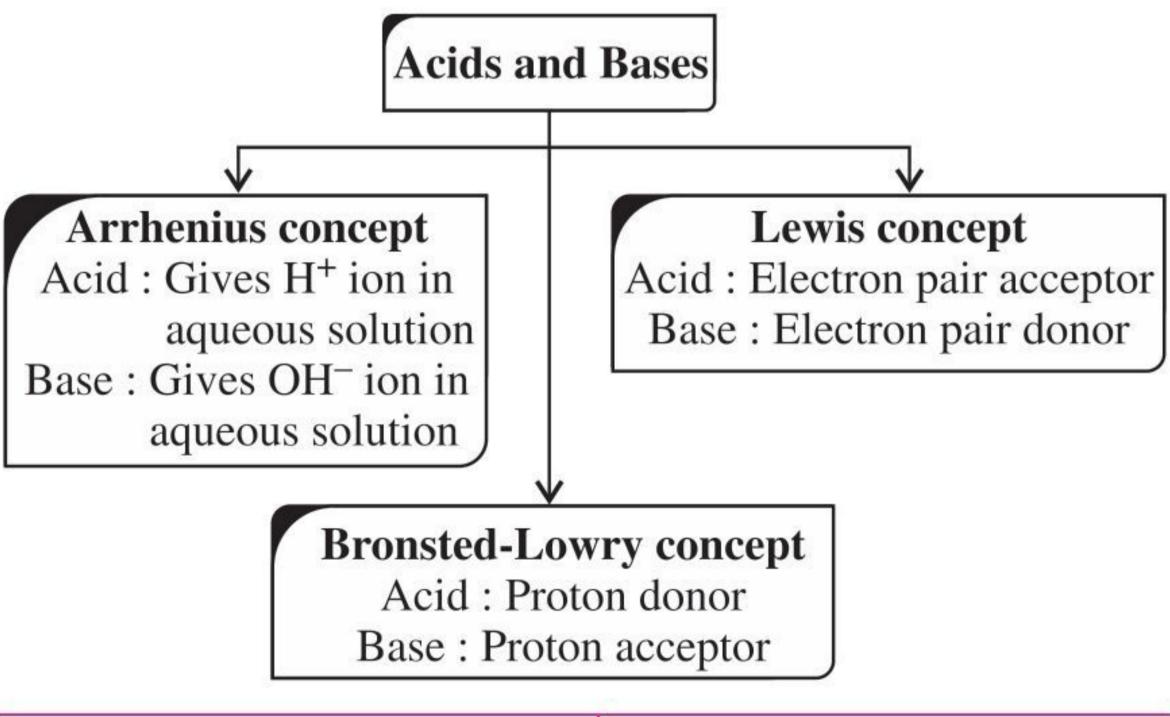
where,  $K_a$  is called dissociation or ionisation constant.

For a weak electrolyte,  $\alpha <<<1$  and  $1-\alpha \approx 1$ 

$$K_a = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{C}} \text{ or } \alpha = \sqrt{K_a V}$$

where, V is the volume containing one mole of electrolyte.

#### ACIDS AND BASES



Strong acids : e.g., HCl, H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub>	Weak acids : e.g.,CH <sub>3</sub> COOH, H <sub>2</sub> CO <sub>3</sub>
Strong bases : e.g., NaOH KOH, CsOH	Weak bases : <i>e.g.</i> ,  NH <sub>4</sub> OH, Cu(OH) <sub>2</sub>

#### **Conjugate Acid-Base Pair**

A pair of acid and base, which differs by a proton is known as conjugate acid-base pair.

#### **Ionisation of Acids and Bases**

$$HA \rightleftharpoons H^{+} + A^{-};$$
(Acid)
$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} \text{ and } \alpha = \sqrt{\frac{K_{a}}{C}}$$

$$BOH \rightleftharpoons B^{+} + OH^{-};$$
(Base)
$$K_{b} = \frac{[B^{+}][OH^{-}]}{[BOH]} \text{ and } \alpha = \sqrt{\frac{K_{b}}{C}}$$

Greater the degree of ionisation  $(\alpha)$ , greater is the dissociation constant ( $K_a$  or  $K_b$ ) and stronger is the acid or base.

Polybasic acids and polyacidic bases: Polybasic acids and polyacidic bases ionise stepwise and each step has its own ionisation constant such as  $K_1$ ,  $K_2$ ,  $K_3...$  Higher order ionisation constants  $(K_2, K_3...)$ are smaller than the lower ionisation constant  $(K_1)$ of a polyprotic acid.

$$K = K_1 \times K_2 \times K_3$$
 ... and generally  $K_1 > K_2 > K_3 > ...$ .

Factors affecting acid strength: Strength of an acid (HA) depends on the strength and polarity of the H—A bond.

Size increases

$$HF << HCl << HBr << HI$$

Acid strength increases

Electronegativity increases

 $CH_4 < NH_3 < H_2O < HF$ 

Acid strength increases

The addition of a substance that suppresses the dissociation of weak electrolyte due to the presence of common ion is called common ion effect.

#### SALT HYDROLYSIS

Salt	Hydrolysis	Resulting solution	Hydrolysis constant ( $K_h$ )	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline, pH > 7	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2} [pK_w + pK_a + \log C]$
Strong acid and Weak base	Cationic	Acidic, pH < 7	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2} \left[ pK_w - pK_b - \log C \right]$
Weak acid and Weak base	Anionic and cationic both	Neutral, pH = 7 $(If K_a = K_b)$	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$pH = \frac{1}{2} \left[ pK_w + pK_a - pK_b \right]$

#### Calculation of pH and pOH in Different Types of Solutions

	Types of solution	Formula
1.	Dilute aqueous solution of a strong acid or a strong base	$pH = -log \{ [H^+]_{acid} + [H^+]_{H_2O} \}$ $pOH = -log \{ [OH^-]_{base} + [OH^-]_{H_2O} \}$
2.	Highly concentrated solution of a strong acid or a strong base (concentration > 1 M)	pH of acidic solution is taken as 0. pH of basic solution is taken as 14.
3.	Solution of a weak acid or a weak base	pH = $-\log (C\alpha) = -\log \sqrt{K_a C}$ pOH = $-\log (C\alpha) = -\log \sqrt{K_b C}$
4.	Mixture of two or more strong monoprotic acids or strong bases	$pH = -log\left(\frac{\Sigma NV}{\Sigma V}\right)$ , $pOH = -log\left(\frac{\Sigma NV}{\Sigma V}\right)$

5.	Mixture of an acid and a base	$pH = -\log\left(\frac{(N_1V_1)_{acid} - (N_2V_2)_{base}}{V_1 + V_2}\right)$ (If acid is in excess.) $pOH = -\log\left(\frac{(N_2V_2)_{base} - (N_1V_1)_{acid}}{V_1 + V_2}\right)$ (If base is in excess.)
6.	Amphiprotic system	$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

#### SOLUBILITY PRODUCT

• A solid salt of the general formula,  $A_x B_y$  with molar solubility 'S' in equilibrium with its saturated solution may be represented by the equation:

$$A_x B_y \Longrightarrow x A^{y+} + y B^{x-}$$

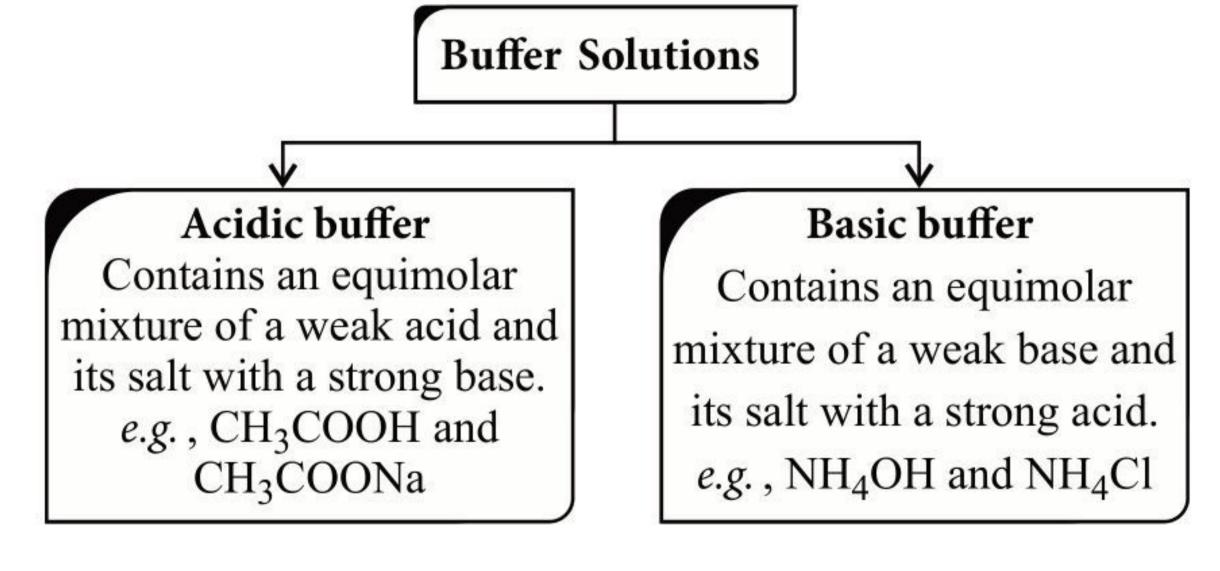
$$K = \frac{[A^{y+}]^{x}[B^{x-}]^{y}}{[A_{x}B_{y}]} ; K[A_{x}B_{y}] = [A^{y+}]^{x}[B^{x-}]^{y}$$

:  $[A_x B_y]$  in solid state remains constant,

$$A^{y+}$$
  $[A^{y+}]^x [B^{x-}]^y = K_{sp}$ .

•  $K_{sp}$  is given by  $Q_{sp}$ , when the concentration of one or more species is not the concentration under equilibrium, and under equilibrium conditions  $K_{sp} = Q_{sp}$ .

Salt type	Relation between $K_{sp}$ and $S$	Examples
$AB_2$	$K_{sp} = (S)(2S)^2 = 4S^3$	PbCl <sub>2</sub> , HgCl <sub>2</sub>
$A_2B$	$K_{sp} = (2S)^2(S) = 4S^3$	Ag <sub>2</sub> CrO <sub>4</sub> , Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Ag <sub>2</sub> SO <sub>4</sub>
$AB_3$	$K_{sp} = (S)(3S)^3 = 27S^4$	Fe(OH) <sub>3</sub> , Al(OH) <sub>3</sub> , Cr(OH) <sub>3</sub>
$A_3B_2$	$K_{sp} = (3S)^3 (2S)^2 = 108S^5$	$Ca_{3}(PO_{4})_{2}, Zn_{3}(PO_{4})_{2}$
AB	$K_{sp} = (S)(S) = S^2$	AgCl, AgBr, PbSO <sub>4</sub> , BaSO <sub>4</sub> , ZnS



• pH of an acidic buffer:

pH=p
$$K_a$$
+log  $\frac{[Salt]}{[Acid]}$  = p $K_a$  + log  $\frac{[Conjugate base]}{[Acid]}$ 

(Henderson—Hasselbalch equation)

pH of a basic buffer:

$$pOH = pK_b + log \frac{[Salt]}{[Base]}$$
$$= pK_b + log \frac{[Conjugate acid]}{[Base]}$$

$$pH = 14 - pOH$$

#### **ANSWERS NOVEMBER 2022: WORD GRID**

А	C	E		1	C	А	N	Н	Υ	D	К	ı	D	E)	
C	Υ	N	М	K	Υ	С	W	G	0	1	Е	Α	0	Р	R
Υ	А	D	N	Α	W	D	Χ	F	L	L	D	N	Α	Q	Α
W	N	Α	Р		Χ	F	Υ	Е	K	U	Υ	М	В	S	N
S	1	С	Q	А	Χ	G	Z	D	Α	Т	Χ	D	С	W	Q
Т	D	D	0	С	М	Н	В	С	R	1	W	L	Е	Z	U
U	E	Е	R	Т	N	J	L	М	М	0	Υ	K	F	R	L
D	R	Z	S	0	0	K	0	Ν	Α	z	Z	G	Н	М	L
Е	W	Υ	Т	S	М	Р	Q	R	S	T	U	J	1	N	1
N	Х	E	L	E	C	T	R	0	Р	Н	1	L	E	R	Z
Т	В	N	F	Х	U	U	С	С	D	В	Α	Χ	W	T	Е
Υ	С	L	T	Υ	R	U	-	Ν	D	1	С	Α	T	0	R
W	D	А	U	Z	1	٧	W	Υ	В	N	М	L	J	Н	F
Χ	Е	R	W	T	E	Χ	Z	А	0	С	D	Е	K	I	G

- 1. Curie
- 5. Indicator
- 2. Cyanide
- 6. Lactose
- 3. Electrophile
- 7. Tranquilizer
- 4. Dilution
- 8. Acetic Anhydride

Winner: Ananya Goswami

### WRAPit up!

#### MCQs TYPE QUESTIONS

- 1. If  $K_{sp(AgCNS)} = 1 \times 10^{-12}$  and  $K_{sp(AgBr)} = 5 \times 10^{-13}$ , then the values of simultaneous solubility of AgCNS and AgBr in a solution of water will be
  - (a)  $8.16 \times 10^{-7}$ ,  $4.08 \times 10^{-7}$
  - (b)  $4.08 \times 10^{-7}$ ,  $8.16 \times 10^{-7}$
  - (c) 8.16, 4.08
  - (d)  $1 \times 10^{-12}$ ,  $5 \times 10^{-13}$
- 2. 0.20 mole of NH<sub>4</sub>Cl are introduced into an empty container of 10 litre and heated to 327 °C to attain equilibrium as:

 $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$ ;  $K_p = 0.36$  atm<sup>2</sup>. The quantity of solid NH₄Cl left is

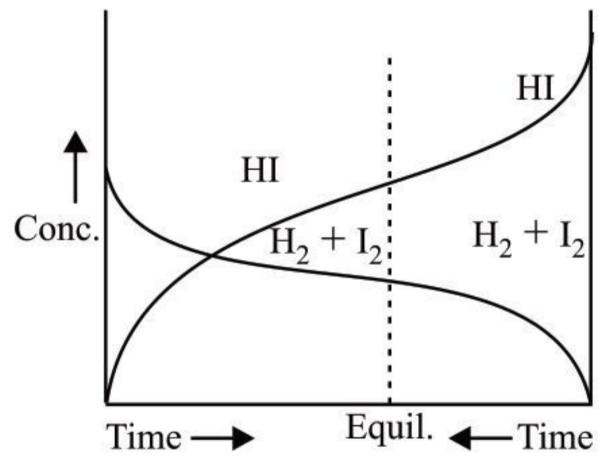
- (a) 0.02 mole
- (b) 0.078 mole
- (c) 0.095 mole
- (d) 0.035 mole.
- 3. If  $K_1$  and  $K_2$  are the respective equilibrium constants for the two reactions,

$$XeF_{6(g)} + H_2O_{(g)} \rightleftharpoons XeOF_{4(g)} + 2HF_{(g)}$$
  
 $XeO_{4(g)} + XeF_{6(g)} \rightleftharpoons XeOF_{4(g)} + XeO_3F_{2(g)}$ 

The equilibrium constant for the reaction,

$$XeO_{4(g)} + 2HF_{(g)} \rightleftharpoons XeO_3F_{2(g)} + H_2O_{(g)}$$
 is

- (a)  $K_1K_2$  (b)  $K_1/K_2^2$
- (c)  $K_2 / K_1$
- (d)  $K_1/K_2$
- Consider the following graph and mark the correct statement.



- (a) Chemical equilibrium in the reaction,  $H_2 + I_2 \Longrightarrow 2HI$  can be attained from either directions.
- (b) Equilibrium can be obtained when H<sub>2</sub> and I<sub>2</sub> are mixed in an open vessel.
- (c) The concentrations of H<sub>2</sub> and I<sub>2</sub> keep decreasing while concentration of HI keeps increasing with time.
- (d) We can find out equilibrium concentration of H<sub>2</sub> and I<sub>2</sub> from the given graph.

Match the column I with column II and mark the appropriate choice.

	Column I	Column II			
(A)	Liquid ⇌ Vapour	(i)	Saturated solution		
(B)	Solid <del>←</del> Liquid	(ii)	Boiling point		
(C)	Solid <del>←</del> Vapour	(iii)	Sublimation point		
(D)	Solute( $s$ ) $\rightleftharpoons$ Solute(solution)	(iv)	Melting point		

- (a)  $(A) \rightarrow (i)$ ,  $(B) \rightarrow (iii)$ ,  $(C) \rightarrow (ii)$ ,  $(D) \rightarrow (iv)$
- (b)  $(A) \rightarrow (ii), (B) \rightarrow (iv), (C) \rightarrow (iii), (D) \rightarrow (i)$
- (c)  $(A) \rightarrow (iv), (B) \rightarrow (ii), (C) \rightarrow (i), (D) \rightarrow (iii)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (ii), (D)  $\rightarrow$  (i)
- 6. For a reaction,  $2\text{NOCl}_{(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$ ,  $K_c$  at  $427 \,^{\circ}\text{C}$  is  $3 \times 10^{-6} \,^{\circ}\text{L}$  mol<sup>-1</sup>. The value of  $K_p$  is nearly

  - (a)  $7.5 \times 10^{-5}$  (b)  $2.5 \times 10^{-5}$
  - (c)  $2.5 \times 10^{-4}$  (d)  $1.72 \times 10^{-4}$
- 7. A solution is 0.1 M with respect to Ag<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup>. Which will precipitate at lowest concentration of PO<sub>4</sub><sup>3-</sup> ion when Na<sub>3</sub>PO<sub>4</sub> solution is added?
  - (a)  $Ag_3PO_4(K_{sp} = 1 \times 10^{-6})$
  - (b)  $Ca_3(PO_4)_2(K_{sp} = 1 \times 10^{-33})$
  - (c)  $Mg_3(PO_4)_2(K_{sp} = 1 \times 10^{-24})$
  - (d) AlPO<sub>4</sub> $(K_{sp} = 1 \times 10^{-20})$
- 8.  $\frac{K_p}{}$  for following reaction will be

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \to CO_{2(g)}$$
(a)  $RT$  (b)  $\frac{1}{RT}$  (c)  $\frac{1}{\sqrt{RT}}$  (d)  $\frac{RT}{2}$ 

- The value of  $K_c$  for the following equilibrium is  $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ . Given  $K_p = 167$  bar at 1073 K.

  - (a)  $1.896 \text{ mol L}^{-1}$  (b)  $4.38 \times 10^{-4} \text{ mol L}^{-1}$
  - (c)  $6.3 \times 10^4 \text{ mol L}^{-1}$  (d)  $6.626 \text{ mol L}^{-1}$
- 10. Reversible reaction is studied graphically as shown in the given figure.  $N_2O_4 \rightleftharpoons 2NO_2, K_c = 4$ Select the correct statements out of I, II and III.

- Reaction quotient has maximum value at point A.
- II. Reaction proceeds left to right at a point when  $[N_2O_4] = [NO_2] = 0.1 M.$
- III.  $K_c = Q$  when point D or F is reached.
- (a) I, II
- (b) II, III (c) I, III
- (d) I, II, III
- 11. Which of the following will produce a buffer solution when mixed in equal volumes?
  - (a) 0.1 mol dm<sup>-3</sup> NH₄OH and 0.1 mol dm<sup>-3</sup> HCl
  - (b) 0.05 mol dm<sup>-3</sup> NH₄OH and 0.1 mol dm<sup>-3</sup> HCl
  - (c)  $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{OH}$  and  $0.05 \text{ mol dm}^{-3} \text{ HCl}$
  - (d) 0.1 mol dm<sup>-3</sup> CH<sub>3</sub>COONa and 0.1 mol dm<sup>-3</sup> NaOH
- 12. A buffer solution contains 0.1 mole of sodium acetate dissolved in 1000 cm<sup>3</sup> of 0.1 M acetic acid. To the above buffer solution, 0.1 mole of sodium acetate is further added and dissolved. The pH of the resulting buffer is
  - (a)  $pK_a$
- (b)  $pK_a + 2$
- (c)  $pK_a \log 2$  (d)  $pK_a + \log 2$
- 13. Assertion: The reaction,

 $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$  is favoured in the forward direction with increase of pressure.

**Reason:** The reaction is exothermic.

- (a) Both assertion and reason are true and reason is the correct explanation of assertion.
- (b) Both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) Assertion is true but reason is false.
- (d) Both assertion and reason are false.
- 14. If  $K_{sp}$  of MOH is  $1 \times 10^{-10}$ , then pH of its aqueous solution will be
  - (a) 3
- (b) 6 (c) 9
- (d) 12
- 15. Solid  $Ba(NO_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4}$  M Na<sub>2</sub>CO<sub>3</sub> solution. At what concentration of Ba<sup>2+</sup> will a precipitate begin to form?  $(K_{sp} \text{ for BaCO}_3 = 5.1 \times 10^{-9})$ 

  - (a)  $4.1 \times 10^{-5} \,\mathrm{M}$  (b)  $5.1 \times 10^{-5} \,\mathrm{M}$

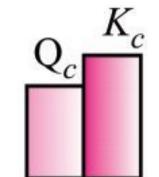
  - (c)  $8.1 \times 10^{-8} \,\mathrm{M}$  (d)  $8.1 \times 10^{-7} \,\mathrm{M}$
- 16. Statement-I: The equilibrium constant is fixed and it is a characteristic for any given chemical reaction at a specified temperature.
  - Statement-II: The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants.
  - (a) Both statement-I and statement-II are true and statement-II is the correct explanation of statement-I.

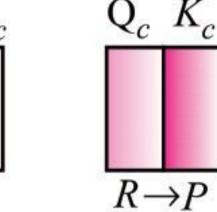
- (b) Both statement-I and statement-II are true but statement-II is not the correct explanation of statement-I.
- (c) Statement-I is true but statement-II is false.
- (d) Both statement-I and statement-II are false.
- 17. At 500 K, the equilibrium constant for the reaction  $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$  is 24.8. If  $\frac{1}{2}$  mol/L of HI is present at equilibrium, what are the concentrations of H<sub>2</sub> and I<sub>2</sub>, assuming that we started by taking HI and reached the equilibrium at 500 K?

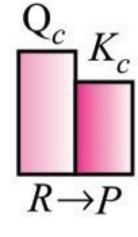
  - (a)  $0.068 \text{ mol L}^{-1}$  (b)  $1.020 \text{ mol L}^{-1}$
  - (c)  $0.10 \text{ mol } L^{-1}$

statement.

- (d)  $1.20 \text{ mol } L^{-1}$
- 18. Predict the direction of the reaction from the comparison of Q<sub>c</sub> and  $K_c$ . Mark the incorrect







- (a) If  $Q_c < K_c$ , reaction goes from left to right.
- (b) If  $Q_c = K_c$ , reaction goes from right to left.
- (c) If  $Q_c > K_c$ , net reaction goes from right to left.
- (d) If  $Q_c = K_c$ , reactants and products are at equilibrium.
- 19. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	Fe(OH) <sub>3</sub>	(i)	$K_{sp} = s^2$
(B)	$Ag_2CrO_4$	(ii)	$K_{sp}=27s^4$
(C)	CH <sub>3</sub> COOAg	(iii)	$K_{sp} = 108s^5$
(D)	$Ca_3(PO_4)_2$	(iv)	$K_{sp}=4s^3$

- (a)  $(A) \rightarrow (iii), (B) \rightarrow (ii), (C) \rightarrow (iv), (D) \rightarrow (i)$
- (b)  $(A) \rightarrow (ii), (B) \rightarrow (iv), (C) \rightarrow (i), (D) \rightarrow (iii)$
- (c)  $(A) \rightarrow (i), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (iv)$
- (d) (A)  $\rightarrow$  (iv), (B)  $\rightarrow$  (i), (C)  $\rightarrow$  (iii), (D)  $\rightarrow$  (ii)
- 20. Given below are the dissociation constant values of few acids. Arrange them in order of increasing acidic strength.

 $H_2SO_3 = 1.3 \times 10^{-2}$ ,  $HNO_2 = 4 \times 10^{-4}$ ,

 $CH_3COOH = 1.8 \times 10^{-5}, HCN = 4 \times 10^{-10}$ 

- (a)  $HCN < CH_3COOH < HNO_2 < H_2SO_3$
- (b)  $CH_3COOH < HNO_2 < HCN < H_2SO_3$
- (c)  $CH_3COOH < HCN < H_2SO_3 < HNO_2$
- (d)  $HNO_2 < H_2SO_3 < CH_3COOH < HCN$

#### **NUMERICAL VALUE TYPE QUESTIONS**

**21.** The p $K_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionised is \_\_\_\_\_.

- 22. The minimum concentration of  $SO_4^{2-}$  required to precipitate  $BaSO_4$  in a solution containing  $1 \times 10^{-4}$  mole of  $Ba^{2+}$  is  $\times 10^{-6}$  M.  $(K_{sp} \text{ for } BaSO_4 = 4 \times 10^{-10})$
- 23. pH of a saturated solution of magnesium hydroxide in water at 298 K is 10. The solubility of the hydroxide in water at 298 K is  $\_\_\times 10^{-5}$  moL L<sup>-1</sup>.
- 24. The gas  $A_2$  in the left flask allowed to react with gas  $B_2$  present in right flask as  $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)};$   $A_{2(g)} + B_{2(g)} = 2AB_{(g)};$   $A_{2(g)} + B_{2(g)} = 2AB_{(g)};$   $A_{2(g)} + B_{2(g)} = 2AB_{(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{2(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{2(g)} = 2AB_{2(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{2(g)} = 2AB_{2(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{2(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{2(g)};$   $A_{2(g)} + AB_{2(g)} = 2AB_{2(g)};$   $A_{$
- 25. The minimum pH required to prevent the precipitation of ZnS in a solution that is 0.01 M  $\operatorname{ZnCl}_2$  and saturated with 0.10 M  $\operatorname{H}_2$ S is \_\_\_\_\_. (Given :  $K_{sp} = 10^{-21}$ ,  $K_{a_1} \times K_{a_2} = 10^{-20}$ )

#### **SOLUTIONS**

- 1. (a)
- 2. **(b):** NH<sub>4</sub>Cl<sub>(s)</sub>  $\rightleftharpoons$  NH<sub>3(g)</sub> + HCl<sub>(g)</sub> moles at t = 0 0.20 0 0 moles at eq. (0.20 - a) a a

  Also,  $K_p = p_{\text{NH}_3} \times p_{\text{HCl}} = p^2$   $p = \sqrt{K_p} = \sqrt{0.36} = 0.6 \text{ atm}$   $p = 0.6 \text{ atm}, V = 10 \text{ L}, R = 0.0821 \text{ L atm mol}^{-1}\text{K}^{-1},$  T = 600 K  $pV = nRT \Longrightarrow 0.6 \times 10 = n \times 0.0821 \times 600$
- n = 0.1218;  $n \text{ of NH}_4\text{Cl left} = 0.2 0.1218 = 0.078 \text{ mole}$ 3. (c):  $K_1 = \frac{[\text{XeOF}_4][\text{HF}]^2}{[\text{XeF}_6][\text{H}_2\text{O}]}$  ...(i)

$$K_2 = \frac{[\text{XeOF}_4][\text{XeO}_3\text{F}_2]}{[\text{XeO}_4][\text{XeF}_6]}$$
...(ii)

Dividing Eq. (ii) by (i) we have,

$$\frac{K_2}{K_1} = \frac{[XeO_3F_2][H_2O]}{[XeO_4][HF]^2} = K'$$

- 4. (a): Equilibrium can be attained by either side of the reactions of equilibrium.
- 5. (b): (A) Liquid  $\rightleftharpoons$  Vapour; equilibrium exists at the boiling point.

  - (C) Solid  $\rightleftharpoons$  Vapour; equilibrium exists at the sublimation point.
  - (D) Solute<sub>(s)</sub>  $\rightleftharpoons$  Solute(solution) equilibrium exists in a saturated solution.

- 6. (d):  $2\text{NOCl}_{(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$   $\Delta n_{(g)} = 3 - 2 = 1$   $K_p = K_c (RT)^{\Delta n_{(g)}} = (3 \times 10^{-6}) \times (0.0821 \times 700)$  $= 172.41 \times 10^{-6} = 1.72 \times 10^{-4}$
- 7. (d): (a)  $Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{3-}$   $K_{sp} = [Ag^+]^3[PO_4^{3-}]$   $[PO_4^{3-}] = \frac{K_{sp}}{(0.1)^3} = \frac{1 \times 10^{-6}}{10^{-3}} = 10^{-3}M$ (b)  $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$ 
  - (b)  $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$   $K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$   $10^{-33} = (0.1)^3 [PO_4^{3-}]^2$   $[PO_4^{3-}]^2 = \frac{10^{-33}}{10^{-3}} = 10^{-30}$ 
    - $[PO_4^{3-}] = 10^{-15} M$
  - (c)  $Mg_3(PO_4)_2 \rightleftharpoons 3Mg^{2+} + 2PO_4^{3-}$  (0.1) $(PO_4^{3-})^2 = \frac{10^{-24}}{10^{-3}} = 10^{-21}$
  - $[PO_4^{3-}] = 3.16 \times 10^{-11} \text{ M}$ (d)  $AlPO_4 \rightleftharpoons Al^{3+} + PO_4^{3-}$ (0.1)

$$\left[PO_4^{3-}\right] = \frac{K_{sp}}{0.1} = \frac{10^{-20}}{0.1} = 10^{-19} M$$

Lower the value of  $K_{sp}$ , lower will be solubility and will precipitate out first.

8. (c):  $\Delta n_g = n_p - n_r = 1 - \frac{3}{2} = \frac{-1}{2}$ 

Hence, 
$$K_p = K_c (RT)^{-1/2}$$
;  $\frac{K_p}{K_c} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{RT}}$ 

9. (a):  $K_p = K_c(RT)^{\Delta n}$ ;  $K_p = 167 \text{ bar}$ ,  $\Delta n = 1$   $K_c = \frac{167 \text{ bar}}{0.0821 \text{ L bar K}^{-1} \text{mol}^{-1} \times 1073 \text{ K}} = 1.896 \text{ mol L}^{-1}$ 

#### mtG

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10. (b): (I) 
$$Q = \frac{[NO_2]^2}{[N_2O_4]}$$

Since,  $[NO_2]$  is minimum and  $[N_2O_4]$  is maximum at point A, hence Q is minimum at this point. Thus, false.

(II) 
$$Q = \frac{(0.1)^2}{(0.1)} = 0.1 < K_c$$

Thus, reaction proceeds left to right. Thus, true. (III)  $K_c = Q$  when equilibrium is reached at point D or F. Thus, true.

- 11. (c): In option (c), all HCl will be neutralised and NH<sub>4</sub>Cl will be formed. Also, some NH<sub>4</sub>OH will be left unneutralised. Thus, the final solution will contain NH<sub>4</sub>OH and NH<sub>4</sub>Cl and it will form a buffer.
- 12. (d): Number of moles of acetic acid = 0.1 molTotal number of moles of sodium acetate present in buffer solution = 0.1 + 0.1 = 0.2 mol

$$\therefore pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= pK_a + \log \frac{0.2}{0.1} = pK_a + \log 2$$

$$\therefore pH = pK_a + \log 2$$

- 13. (b): According to Le Chatelier's principle, with increase of pressure, equilibrium shifts in that direction in which lesser number of moles of gaseous products are produced.
- 14. (c):  $K_{sp}$  of  $MOH = 1 \times 10^{-10}$   $[M^+]$   $[OH^-] = 1 \times 10^{-10}$ Now,  $[M^+] = [OH^-]$   $\therefore$   $[OH^-]^2 = 1 \times 10^{-10}$  or  $[OH^-] = 10^{-5}$  $[H_3O^+] = \frac{10^{-14}}{10^{-5}} = 10^{-9}$ ;  $pH = -\log(10^{-9}) = 9$
- 15. (b):  $K_{sp}$  (BaCO<sub>3</sub>) = [Ba<sup>2+</sup>][CO<sub>3</sub><sup>2-</sup>] = 5.1 × 10<sup>-9</sup> Given, [CO<sub>3</sub><sup>2-</sup>] = 1.0 × 10<sup>-4</sup> M (from Na<sub>2</sub>CO<sub>3</sub>)  $\therefore 5.1 \times 10^{-9} = [Ba^{2+}] \times (10^{-4})$   $\Rightarrow [Ba^{2+}] = 5.1 \times 10^{-5} M$ Thus, when [Ba<sup>2+</sup>] = 5.1 × 10<sup>-5</sup> M, BaCO<sub>3</sub> precipitate will begin to form.
- 16. (c): The equilibrium constant is always fixed and it is a characteristic of a reaction at specified temperature. It defines the composition of the final equilibrium mixture of that reaction, regardless of the starting amount of reactants and products.

17. (c): 
$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}; \quad K_c = 1/24.8$$
Initial conc. 1 0 0
At equilibrium 0.5  $x$   $x$ 

$$K_c = \frac{[H_2][I_2]}{[HI]^2} \text{ or } \frac{1}{24.8} = \frac{x.x}{0.5 \times 0.5} \text{ or } x^2 = \frac{0.25}{24.8} = 0.010$$
  
 $x = 0.10 \text{ mol L}^{-1}$ 

18. (b): If  $Q_c = K_c$ , reaction is in equilibrium.

19. (b): (A) 
$$Fe(OH)_3 \longrightarrow Fe^{3+} + 3OH^-$$
;  $K_{sp} = 27s^4$ 

(B) 
$$Ag_2CrO_4 \Longrightarrow 2Ag^+ + CrO_4^{(2s)^2}$$
;  $K_{sp} = 4s^3$ 

(C) 
$$CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+$$
;  $K_{sp} = s^2$ 

(D) 
$$Ca_3(PO_4)_2 \Longrightarrow 3Ca^{2+} + 2PO_4^{3-}; K_{sp} = 108s^5$$

20. (a)

21. (9.5): For buffer solution,

pH = p
$$K_a$$
 + log  $\left[\frac{\text{Salt}}{\text{Acid}}\right]$  = 4.5 + log  $\left[\frac{\text{Salt}}{\text{Acid}}\right]$ 

As HA is 50% ionised, hence [Salt] = [acid] pH =  $4.5 \Rightarrow$  pOH = 14 - 4.5 = 9.5

22. (4): BaSO<sub>4</sub> 
$$\rightleftharpoons$$
 Ba<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup>
Conc.:  $1 \times 10^{-4}$  s
$$K_{sp} = 4 \times 10^{-10}; \ 4 \times 10^{-10} = 1 \times 10^{-4} \times s$$

$$s = \frac{4 \times 10^{-10}}{1 \times 10^{-4}} = 4 \times 10^{-6} M$$

23. (5): 
$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$
  
 $s \qquad 2s$ 

pH of  $Mg(OH)_2$  solution is 10.

$$\therefore \quad pOH = 4; \quad So, [OH^-] = 10^{-4}$$
$$[OH^-] = 2 \times solubility$$

:. Solubility = 
$$\frac{10^{-4}}{2}$$
 =  $0.5 \times 10^{-4} = 5 \times 10^{-5} \text{ mol L}^{-1}$ 

24. (0.66): 
$$A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$$
  
Initial moles 2 4 0  
Moles at eq.  $2-x$   $4-x$   $2x$   
 $K_c = \frac{4x^2}{(2-x)(4-x)} = 4 \Rightarrow x = 1.33$  mole
$$[AB_{(g)}] = \frac{2 \times 1.33}{4} = 0.66 \text{ M}$$

25. (1): 
$$K_{sp} = [Zn^{2+}][S^{2-}]$$
  
 $[S^{2-}] = \frac{10^{-21}}{0.01} = 10^{-19}$   
 $H_2S \rightleftharpoons H^+ + HS^-$ ;  $K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$   
 $HS^- \rightleftharpoons H^+ + S^{2-}$ ;  $K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]}$   
 $K_{a_1} \cdot K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$ ;  $10^{-20} = \frac{[H^+]^2 \times 10^{-19}}{0.1}$   
 $\Rightarrow [H^+] = 0.1 \text{ or pH} = 1$ 



# Warm-up!

Chapterwise practice questions for CBSE Exams as per the latest pattern and reduced syllabus by CBSE for the academic session 2022-23.

Series-5

**Redox Reactions | Organic Chemistry-**Some Basic Principles and Techniques

Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

#### Read the following instructions carefully.

- There are 35 questions in this question paper with internal choice.
- SECTION A consists of 18 multiple-choice questions carrying 1 mark each. (b)
- SECTION B consists of 7 very short answer questions carrying 2 marks each. (c)
- SECTION C consists of 5 short answer questions carrying 3 marks each. (d)
- SECTION D consists of 2 case-based questions carrying 4 marks each. (e)
- SECTION E consists of 3 long answer questions carrying 5 marks each. (f)
- All questions are compulsory. (g)
- Use of log tables and calculators is not allowed.

#### **SECTION A**

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

- 1. Highest oxidation state of Mn is present in
  - (a)  $KMnO_4$
- (b)  $K_2MnO_4$
- (c)  $Mn_2O_3$
- (d)  $MnO_2$
- Chemical formula of Prussian blue is

  - (a)  $Na_4[Fe(CN)_6]$  (b)  $K_4[Fe(CN)_6]$

  - (c)  $Fe_4[Fe(CN)_6]_3$  (d) None of these.
- The element that does not severally show positive oxidation state is
  - (a) Mg
- (b) Na
- (c) Ca
- Among the following, the true property about  $H_3C$   $\rightarrow CH_3$  is
  - (a) non-polar
  - (b)  $sp^2$ -hybridised
  - (c) electrophile can attack C<sup>+</sup>
  - (d) does not undergo hydrolysis.

- 5. In which of the following compounds, the carbon marked with asterisk is expected to have greatest positive charge?

  - (a)  $\check{C}H_3$ — $CH_2$ —Cl (b)  $\check{C}H_3$ — $CH_2$ — $Mg^+Cl^-$  (c)  $\check{C}H_3$ — $CH_2$ —Br (d)  $\check{C}H_3$ — $CH_2$ — $CH_3$
- The IUPAC name of the compound

- (a) 1,2,3-tricarboxy-2,1-propane
- (b) 3-carboxy-3-hydroxy-1,5-pentanedioic acid
- (c) 3-hydroxy-3-carboxy-1,5-pentanedioic acid
- (d) None of these.
- $aC_2H_{6(g)} + nO_2 \rightarrow bCO_{2(g)} + mH_2O_{(l)}$ In this equation, ratio of the coefficients of CO<sub>2</sub> and  $H_2O$  is
  - (a) 1:1

- (b) 2:3 (c) 3:2 (d) 1:3

- 8. Stability of alkyl carbocations can be explained by
  - (a) inductive effect only
  - (b) hyperconjugation only
  - (c) both inductive effect and hyperconjugation
  - (d) electromeric effect only.
- 9. Amongst the given reactions, redox reaction is
  - (a)  $C + O_2 \longrightarrow CO_2$
  - (b)  $2\text{NaH} \xrightarrow{\Delta} 2\text{Na} + \text{H}_2$
  - (c) Fe + 2HCl  $\longrightarrow$  FeCl<sub>2</sub> + H<sub>2</sub>
  - (d) All of these.
- 10. In which of the following pairs, there is maximum difference in the oxidation number of the underlined elements?
  - (a)  $\underline{NO}_2$  and  $\underline{N}_2O_4$
- (b)  $\underline{P}_2O_5$  and  $\underline{P}_4O_{10}$
- (c)  $N_2O$  and NO
- (d)  $\underline{SO}_2$  and  $\underline{SO}_3$
- 11. The bond order of individual carbon-carbon bonds in benzene is
  - (a) one
- (b) two
- (c) between one and two
- (d) one and two alternately.
- 12. In the standardization of  $Na_2S_2O_3$  using  $K_2Cr_2O_7$  by iodometry, the equivalent weight of  $K_2Cr_2O_7$  is
  - (a) (Molecular weight)/2
  - (b) (Molecular weight)/6
  - (c) (Molecular weight)/3
  - (d) same as molecular weight.
- 13. The non existence of PbI<sub>4</sub> and PbBr<sub>4</sub> is due to
  - (a) highly oxidizing nature of Pb<sup>4+</sup> ions
  - (b) highly reducing nature of I and Br ions
  - (c) larger size of Pb<sup>4+</sup>, Br<sup>-</sup> and I<sup>-</sup> ions
  - (d) both (a) and (b).
- 14. Empirical formula of a compound is CH<sub>2</sub>O and its molecular mass is 90, the molecular formula of the compound is
  - (a)  $C_3H_6O_3$
- (b)  $C_2H_4O_2$
- (c)  $C_6H_{12}O_6$
- (d)  $CH_2O$
- 15. Given below are two statements labelled as Assertion (A) and Reason (R).
- **Assertion (A):** The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.
  - **Reason** (**R**): The oxygen of peroxide is in -1 oxidation state and it is converted to zero oxidation state in  $O_2$  and -2 oxidation state in  $H_2O$ .
  - Select the most appropriate answer from the options given below:
  - (a) Both A and R are true and R is the correct explanation of A.
  - (b) Both A and R are true but R is not the correct explanation of A.

- (c) A is true but R is false.
- (d) A is false but R is true.
- 16. Given below are two statements labelled as Assertion (A) and Reason (R).
  - **Assertion (A):** Components of a mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography.
  - **Reason** (R): The coloured components of inks migrate at different rates because paper selectively retains different components according to the difference in their partition between the two phases. Select the most appropriate answer from the options given below:
  - (a) Both A and R are true and R is the correct explanation of A.
  - (b) Both A and R are true but R is not the correct explanation of A.
  - (c) A is true but R is false.
  - (d) A is false but R is true.
- 17. Given below are two statements labelled as Assertion (A) and Reason (R).

**Assertion**: In the representation,

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ}$$
 and  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$ ,

Fe<sup>3+</sup>/Fe<sup>2+</sup> and Cu<sup>2+</sup>/Cu are redox couples.

**Reason**: Redox couple is the combination of oxidised and reduced form of a substance involved in an oxidation or reduction half cell.

Select the most appropriate answer from the options given below:

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.
- 18. Given below are two statements labelled as Assertion (A) and Reason (R).

**Assertion (A):** Energy of resonance hybrid is equal to the average of energies of all canonical forms.

**Reason (R):** Resonance hybrid cannot be presented by a single structure.

Select the most appropriate answer from the options given below:

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

#### **SECTION B**

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

- 19. Find the oxidation number of underlined elements:
  - (a)  $K_2MnO_4$
- **(b)** KAl( $\underline{SO}_4$ )<sub>2</sub>.12H<sub>2</sub>O
- 20. Draw structures of
  - (a) 3, 4-dimethylphenol (b) 6-hydroxyheptanal.

#### OR

In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the % of Br in the compound.

(At. mass of Ag = 108, Br = 80)

21. Explain the statement 'oxidation and reduction are reciprocal'.

#### OR

Balance the following equation in basic medium by ion-electron method:

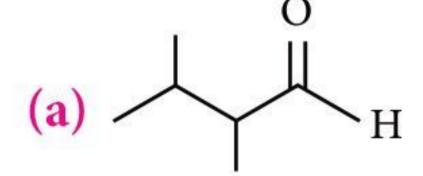
$$P_{4(s)} + OH_{(aq)}^- \longrightarrow PH_{3(g)} + H_2PO_{2(aq)}^-$$

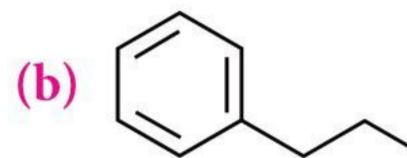
- 22. An iron rod is immersed in solution containing 1.0 M NiSO<sub>4</sub> and 1.0 M ZnSO<sub>4</sub>. Predict giving reasons which of the following reactions is likely to proceed.
  - (a) Fe reduces Zn<sup>2+</sup> ions
  - (b) Fe reduces Ni<sup>2+</sup> ions. (Given:  $E^{\circ}_{Zn^{2+}/Zn} = -0.76 \text{ V}, E^{\circ}_{Fe^{2+}/Fe} = -0.44 \text{ V}$ and  $E^{\circ}_{Ni}^{2+}_{/Ni} = -0.25 \text{ V}$
- 23. (a) Mention the type of hybridisation of each carbon in the compound  $CH_3$ —CN.
  - (b) Draw the structure of 2-methylpropan-2-ol.
- 24. Identify the oxidant and reductant in the following reactions:

(a) 
$$\operatorname{Zn}_{(s)} + \frac{1}{2} \operatorname{O}_{2(g)} \longrightarrow \operatorname{ZnO}_{(s)}$$

(b) 
$$Zn_{(s)} + 2H^{+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

25. Give IUPAC name of the following compounds.





#### SECTION C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

- 26. Give the balanced equations for the reactions that form the basis for the following redox titrations:
  - (a) titration of potassium permanganate for estimation of ferrous ions.

- (b) titration of iodine against sodium thiosulphate (iodometric titration).
- iodometric titration for estimation of cupric ions.
- 27. The following techniques are used to quantitatively estimate extra elements in organic compound. Identify the name of the method and the element estimated by this method.
  - (a) A known mass of an organic compound is heated with fuming HNO<sub>3</sub> in presence of AgNO<sub>3</sub>.
  - (b) Organic compound is heated with dry copper oxide in atmosphere of  $CO_2$ .
  - (c) Organic compound is heated with conc. H<sub>2</sub>SO<sub>4</sub>.

- Define hyperconjugation effect. Explain why  $(CH_3)_3C^+$  is more stable than  $CH_3CH_2^+$ .
- (b) Identify the nucleophiles from the following:  $R_3$ N, BF<sub>3</sub>, RMgX, NC<sup>-</sup>.
- 28. (a) Balance the following redox reaction by ionelectron method.
  - $MnO_4^- + SO_2 \rightarrow Mn^{2+} + HSO_4^-$  (acidic medium)
  - (b) Identify the oxidant and reductant in the following reaction:

$$2K_4[Fe(CN)_6]_{(aq)} + H_2O_{2(aq)} \rightarrow 2K_3[Fe(CN)_6]_{(aq)} + 2KOH_{(aq)}$$

- 29. How are free radicals, carbocations and carbanions produced? Explain.
- **30.** Give reasons for **any three** of the following:
  - (i) Iron undergoes oxidation more readily than copper.
  - (ii) In an electrochemical cell, an electrode with lower electrode potential acts as a reducing agent.
  - (iii) When a copper rod is placed in silver nitrate solution, the solution becomes hot but the reverse is not true.
  - (iv) Iron reacts with dilute H<sub>2</sub>SO<sub>4</sub> to evolve H<sub>2</sub> gas but Ag does not.

#### SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. Oil India Company is refining petroleum by fractional distillation. It gives petrol, diesel, kerosene and fuel oil which are most useful in transportation and for domestic purposes. Petroproducts are the sources of lot of pollution. Use of CNG and LPG can reduce pollution to some extent. Unleaded petrol, speed petrol and turbo diesel

also reduce pollution. Oil Inida is producing high quality petrol and diesel so as to reduce pollution.

#### Answer the following questions:

- (a) Why should we use less petro-products?
- (b) What is the advantage of unleaded petrol?
- (c) What are advantages of speed/power/premium petrol and turbo diesel?

#### OR

What are the values possessed by Oil India Company?

32. Sonali was discussing a very interesting topic of chemistry 'Redox reactions' with her friend Geeta in the class and planned to search day-to-day life processes which are based on these reactions. They both went home and did their work and made project file. Next day they exchanged their information and were amazed how 'Redox reactions' play major role in our daily life.

#### Answer the following questions:

- (a) Give one example of redox reactions that occur in human and plant body each.
- (b) Is rusting or corrosion a 'redox reaction'? What is electroplating?
- (c) Can we store copper sulphate in an iron vessel? Give reason for your answer.

#### OR

The colour of KI solution containing starch turns blue when it is shaken with cold Cl<sub>2</sub> water. Explain why?

#### **SECTION E**

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

- 33. (a) Suggest a method used to purify the liquids which have high boiling points and decompose below their boiling points.
  - (b) How will you separate a mixture of ammonium chloride and common salt?
  - (c) Will CCl<sub>4</sub> give white precipitate of AgCl on heating with silver nitrate? Give reason for your answer.
  - (d) In the estimation of sulphur, 0.157 g of an organic compound gave 0.4813 g of BaSO<sub>4</sub>. What is the percentage of sulphur in the compound?

(At. wt. of Ba = 137, 
$$S = 32$$
,  $O = 16 u$ )

#### OR

0.45 g of an organic compound gave 0.792 g of  $CO_2$  and 0.324 g of water on combustion. 0.24 g of same substance was Kjedahlised and the NH<sub>3</sub> formed was absorbed in 50.0 cm<sup>3</sup> of  $\frac{M}{8}$  H<sub>2</sub>SO<sub>4</sub>. The excess acid required 77.0 cm<sup>3</sup> of  $\frac{M}{10}$  NaOH for complete neutralisation. Calculate the empirical formula of the compound.

**34.** (a) Balance the following unbalanced equation (in acidic medium) by ion-electron method (half-reaction method).

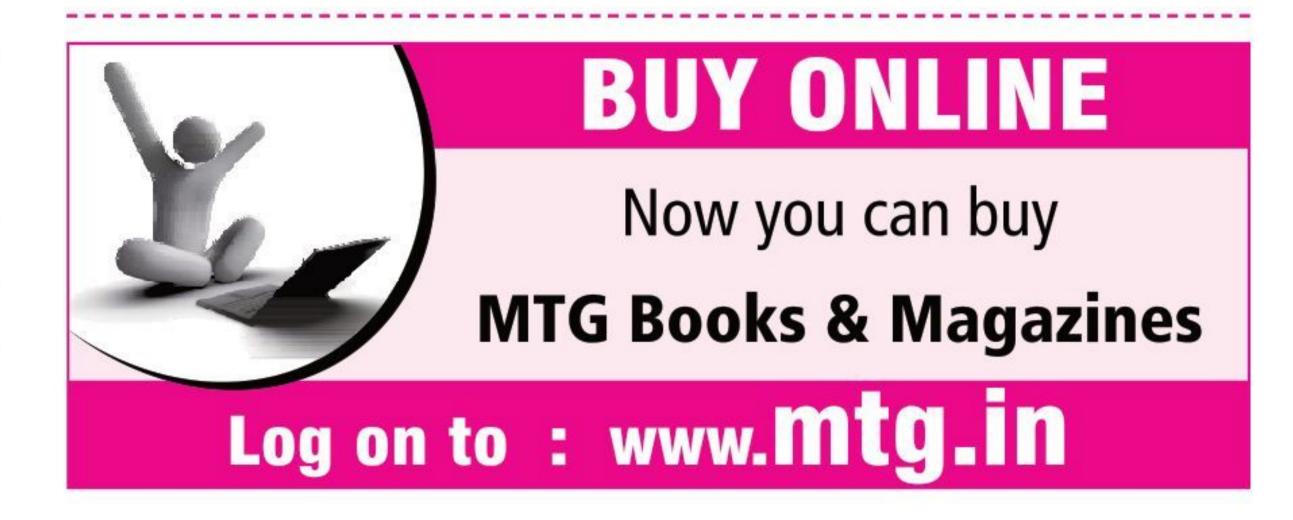
$$\operatorname{Mn}_{(aq)}^{2+} + \operatorname{ClO}_{3(aq)}^{-} \longrightarrow \operatorname{MnO}_{2(s)} + \operatorname{ClO}_{2(aq)}$$

- (b) Explain why sulphur dioxide can act both as an oxidant and reductant but nitric acid can act only as an oxidant.
- (c) What do you understand by disproportionation reaction?

#### OR

Using oxidation number concept, identify the redox reactions. Identify oxidising and reducing agents in case of redox reactions.

- (a)  $H_3PO_{4(aq)} + 3KOH_{(aq)} \longrightarrow K_3PO_{4(aq)} + 3H_2O_{(l)}$
- (b)  $\operatorname{Zn}_{(s)} + 2\operatorname{HCl}_{(aq)} \longrightarrow \operatorname{ZnCl}_{2(aq)} + \operatorname{H}_{2(g)}$
- (c)  $6\text{Fe}^{2+}_{(aq)} + \text{BrO}^{-}_{3(aq)} + 6\text{H}^{+}_{(aq)} \longrightarrow 6\text{Fe}^{3+}_{(aq)} + \text{Br}^{-}_{(aq)} + 3\text{H}_2\text{O}_{(l)}$
- (d)  $2Zn_{(s)} + O_{2(g)} \longrightarrow 2ZnO_{(s)}$
- (e)  $\operatorname{Sn}_{(aq)}^{2+} + \operatorname{IO}_{4(aq)}^{-} \longrightarrow \operatorname{Sn}_{(aq)}^{4+} + \operatorname{I}_{(aq)}^{-}$
- 35. Give condensed and bond-line structural formulae for the following and identify the functional group(s) present (if any).
  - (a) 2, 2,4-trimethylpentane,
  - (b) 2-hydroxy-1, 2, 3-propanetricarboxylic acid,
  - (c) cycloocta-1, 5-diene,
  - (d) hexandial,
  - (e) 2-(4-iso-butylphenyl) propanoic acid.



#### SOLUTIONS

- 1. (a)
- 2. (c):  $Fe^{2+}$  ions are oxidized to  $Fe^{3+}$  which reacts with sodium ferrocyanide to give ferriferrocyanide which is Prussian blue in colour.

 $4\text{Fe}^{3+} + 3\text{Na}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{Na}^+$ Prussian blue

- 3. (d) 4. (b) 5. (a) 6. (b)
- 7. (b): The balanced equation is,  $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Ratio of the coefficients of CO<sub>2</sub> and H<sub>2</sub>O is 4:6 or 2:3.

- 9. (d)
- 12. (b):  $K_2Cr_2O_7$  acts as an oxidising agent in presence of dil.  $H_2SO_4$ .

 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ 

Equivalent weight of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

$$= \frac{\text{Molecular weight}}{\text{Number of electrons gained}} = \frac{M}{6}$$

- 13. (d) 15. (a) 14. (a)
- 17. (a) 18. (d)
- 19. (a) Let the oxidation number of Mn in  $K_2MnO_4$  be x.  $2 \times (+1) + x + (-2) \times 4 = 0 \implies x = +6$
- (b) Let the oxidation number of S in KAl(SO<sub>4</sub>)<sub>2</sub>.  $12H_2O$ be x.

$$\therefore +1+3+2x-16+0=0 \implies 2x-12=0 \implies x=+6$$

$$OH$$

Molar mass of AgBr =  $108 + 80 = 188 \text{ g mol}^{-1}$ 188 g AgBr contains 80 g bromine.

0.12 g AgBr contains  $\frac{80 \times 0.12}{188}$  g bromine.

Percentage of bromine =  $\frac{80 \times 0.12 \times 100}{188 \times 0.15}$  = 34.04 % 21. Oxidation and reduction always take place simultaneously. In the following example, one substance

is oxidised and other is reduced at the same time. Example,

Reduction 
$$\longrightarrow$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Oxidation \longrightarrow$$

HgCl<sub>2</sub> is reduced to Hg<sub>2</sub>Cl<sub>2</sub>, and SnCl<sub>2</sub> is oxidised to SnCl<sub>4</sub>.

 ${\rm P}_{4(s)}^{0} + {\rm OH}_{(aa)}^{-} \longrightarrow {\rm PH}_{3(g)}^{-3} + {\rm H}_{2}^{+1}{\rm PO}_{2(aa)}^{-}$ Oxidation half-reaction,

 $P_4 + 8OH^- \longrightarrow 4H_2PO_2^- + 4e^-$ ...(i)

Reduction half-reaction,

 $12e^{-} + 12H_{2}O_{(aq)} + P_{4(s)} \longrightarrow 4PH_{3(g)} + 12OH^{-}$  ...(ii) On multiplying equation (i) by 3 and adding it to equation (ii), we have balanced equation:

 $3H_2O_{(l)} + P_{4(s)} + 3OH^- \longrightarrow 3H_2PO_{2(aa)}^- + PH_{3(g)}$ 

- 22. (a) Since,  $E^{\circ}$  of Zn is more negative than that of Fe, therefore, Zn will be oxidised to Zn<sup>2+</sup> ions while Fe<sup>2+</sup> ions will be reduced to Fe. In other words, Fe will not reduce Zn<sup>2+</sup> ions.
- (b) Since,  $E^{\circ}$  of Fe is more negative than that of Ni, therefore, Fe will be oxidised to Fe<sup>2+</sup> ions while Ni<sup>2+</sup> ions will be reduced to Ni. Thus, Fe reduces Ni<sup>2+</sup> ions.
- 23. (a)  $\tilde{C}H_3-\tilde{C}\equiv N$ , 1<sup>st</sup> carbon is 'sp' and 2<sup>nd</sup> carbon is sp<sup>3</sup> hybridised.

2-Methylpropan-2-ol

- 24. (a) Zn is reducing agent (reductant) and  $O_2$  is an oxidising agent (oxidant).
- (b) Zn is reducing agent (reductant), whereas H<sup>+</sup> is an oxidising agent (oxidant).
- 25. (a) IUPAC name: 2, 3-Dimethylbutanal
- (b) IUPAC name: 1-Phenylpropane
- 26. (a)  $5Fe_{(aq)}^{2+} + MnO_{4(aq)}^{-} + 8H_{(aq)}^{+} \longrightarrow 5Fe_{(aq)}^{3+} + Mn_{(aq)}^{2+} + 4H_2O_{(l)}$ (b)  $I_{2(aq)} + 2S_2O_{3(aq)}^{2-} \longrightarrow 2I_{(aq)}^{-} + S_4O_{6(aq)}^{2-}$
- (c)  $2Cu_{(aq)}^{2+} + 4I_{(aq)}^{-} \longrightarrow Cu_{2}I_{2(s)} + I_{2(s)}$
- 27. (a) Estimation of halogen by Carius method.
- (b) Estimation of nitrogen by Dumas method.
- Estimation of nitrogen by Kjeldahl's method.

#### OR

- (a) Hyperconjugation involves delocalisation of σ electrons of C-H bond of an alkyl group directly attached to an atom of unsaturated system or sp<sup>2</sup> hybrid carbon. Hyperconjugative interaction in (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> is greater than that in CH<sub>3</sub>CH<sub>2</sub><sup>+</sup> as (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> has nine C—H bonds.
- (b) RMgX,  $R_3N$  and  $NC^-$
- 28. (a)  $MnO_4^- + SO_2 \rightarrow Mn^{2+} + HSO_4^-$  (acidic medium)  $[5e^{-} + 8H^{+} + MnO_{4}^{-} \rightarrow Mn^{2+} + 4H_{2}O]$  $[2H_2O + SO_2 \rightarrow HSO_4^- + 3H^+ + 2e^-]$

 $H^{+} + 2MnO_{4}^{-} + 5SO_{2} + 2H_{2}O \rightarrow 2Mn^{2+} + 5HSO_{4}^{-}$ 

- (b)  $K_4[Fe(CN)_6]$  acts as a reducing agent as oxidation number of Fe is changed from +2 to +3 and  $H_2O_2$  act as an oxidising agent as oxidation number of oxygen is changed from -1 to -2.
- **29.** Free radicals are produced by homolytic fission, *e.g.*;

Carbocations are formed by heterolytic fission, e.g.;

$$CH_3 \xrightarrow{f} Cl \longrightarrow CH_3 + Cl^-$$

Carbanions are formed by abstraction of  $H^+$  by nucleophile from  $\alpha$ -carbon (carbon attached to functional group).

$$CH_3CHO + OH^- \longrightarrow CH_2 - C - H + H_2O$$
Carbanion

- 30. (i) The electrode potential of iron,
- (*i.e.*,  $E^{\circ}_{Fe^{2+}/Fe} = -0.44 \text{ V}$ ) is lower than that of copper (*i.e.*,  $E^{\circ}_{Cu^{2+}/Cu} = +0.34 \text{ V}$ ) and hence Fe has greater tendency to get converted into Fe<sup>2+</sup> ions than Cu. In other words, iron undergoes oxidation more readily than copper.
- (ii) An electrode with lower electrode potential has more tendency to get oxidised. In other words, it has more tendency to release electrons, and hence acts as a reducing agent.
- (iii) Copper ( $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ ) has lower electrode potential than silver ( $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$ ). Therefore, Cu releases electrons and gets oxidised to Cu<sup>2+</sup> ions while Ag<sup>+</sup> ions accept these electrons and get reduced to Ag metal.

$$Cu_{(s)} + 2Ag_{(aq)}^+ \longrightarrow Cu_{(aq)}^{2+} + 2Ag_{(s)}$$

The chemical energy of this reaction appears as heat and hence the solution becomes hot.

Since, the reverse reaction cannot occur (because the  $E^{\circ}$  of Ag is higher than that of Cu).

Therefore, no change is observed.

(iv) Fe has lower electrode potential ( $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$ ) than that of hydrogen ( $E_{\text{H}^{+}/\text{H}_{2}}^{\circ} = 0.0 \text{ V}$ ), therefore, Fe is a better reducing agent than  $H_{2}$  and hence reduces  $H^{+}$  ions to produce  $H_{2}$  gas.

$$Fe_{(s)} + 2H^{+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$$

In contrast, Ag has higher electrode potential  $(E_{Ag^+/Ag}^{\circ} = 0.80 \text{ V})$  than hydrogen. Therefore, H<sub>2</sub> is a better reducing agent than Ag. In other words, Ag cannot reduce H<sup>+</sup> ions to produce H<sub>2</sub> gas.

31. (a) It is because they are the sources of air pollution and we have to import a lot of oil which needs lot of foreign currency.

- (b) It prevents pollution due to lead.
- (c) They are refined to more extent and undergo almost complete combustion and create less pollution.

#### OR

They are helping to reduce pollution by improving quality of diesel and petrol.

**32.** (a) Photosynthesis and respiration are two examples of redox reactions occurring in plant and human body respectively.

$$6CO_2 + 6H_2O + Energy (Sunlight) \xrightarrow{Chlorophyll} \frac{Chlorophyll}{Photosynthesis}$$

$$C_6H_{12}O_6 + 6O_2$$
Glucose

Like photosynthesis, respiration is also a redox reaction in which, glucose is oxidised to  $CO_2$  and  $O_2$  is reduced to  $H_2O$ .

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{Respiration}} 6CO_2 + 6H_2O + \text{Energy}$$
Glucose

- (b) Corrosion (rusting) is a redox reaction. The deposition of one metal over another through electrolysis is called electroplating.
- (c) No, because iron is more reactive than copper, and therefore, it will displace copper from its salt solution.

$$Fe_{(s)} + CuSO_{4(aq)} \longrightarrow FeSO_{4(aq)} + Cu_{(s)}$$

 $Cl_2$  is stronger oxidizing agent than  $I_2$ , therefore, when  $Cl_2$  is passed through KI solution,  $Cl_2$  gets reduced to  $Cl^-$  ions while  $I^-$  ions get oxidised to violet coloured iodine according to the equation,

$$Cl_{2(aq)} + 2I^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + I_{2(s)}$$

The iodine thus produced forms a blue coloured inclusion complex with starch and hence the solution turns blue.

- 33. (a) Distillation under reduced pressure
- (b) Sublimation
- (c) No, it is because CCl<sub>4</sub> is non-polar covalent compound, does not give Cl<sup>-</sup> therefore does not react with AgNO<sub>3</sub> solution.

(d) % of S = 
$$\frac{32}{233} \times \frac{\text{Wt. of BaSO}_4}{\text{Wt. of organic compound}} \times 100$$
  
=  $\frac{32}{233} \times \frac{0.4813}{0.157} \times 100 = 42.10\%$   
OR

% of C = 
$$\frac{12}{44} \times \frac{0.792}{0.45} \times 100 = 48\%$$
  
% of H =  $\frac{2}{18} \times \frac{0.324}{0.45} \times 100 = 8\%$   
 $M_1V_1 = 2M_2V_2 \Rightarrow \frac{1}{10} \times 77 = 2 \times \frac{1}{8} \times V_2 \Rightarrow V_2 = 30.8 \text{ cm}^3$   
(NaOH) (H<sub>2</sub>SO<sub>4</sub>)

Volume of 
$$\frac{M}{8}$$
 H<sub>2</sub>SO<sub>4</sub> consumed by NH<sub>3</sub> = 2(50 – 30.8)  
= 2 × 19.2 cm<sup>3</sup>  
19.2 cm<sup>3</sup> of  $\frac{M}{8}$  H<sub>2</sub>SO<sub>4</sub> = 2 × 19.2 cm<sup>3</sup> of  $\frac{M}{8}$  NH<sub>3</sub>  
% of N =  $\frac{1.4 \times 2 \times V_1 \times M_1}{W}$  =  $\frac{1.4 \times 2 \times 19.2 \times 1}{0.24 \times 8}$  = 28%

Element	%	2000	Relative no. of atoms	and the same of th	-
С	48	12	48/12 = 4	4/1 = 4	4
Н	8	1	8/1 = 8	8/1 = 8	8
N	28	14	28/14 = 2	2/1 = 2	2
О	16	16	16/16 = 4	1/1 = 1	1

Empirical formula =  $C_4H_8N_2O$ 

34. (a) The equation is balanced in terms of number of atoms and the charges. Hence, balanced equation is:  $\operatorname{Mn}_{(aq)}^{2+} + 2\operatorname{ClO}_{3(aq)}^{-} \longrightarrow \operatorname{MnO}_{2(s)} + 2\operatorname{ClO}_{2(aq)}^{-}$ 

(b) In SO<sub>2</sub>, the O.N. of S is +4. In principle, S can have a minimum oxidation state of -2 and a maximum of +6. Therefore, when O.N. of sulphur decreases, it acts as an oxidising agent and when it increases, it acts as a reducing agent. In HNO<sub>3</sub>, N exists in its highest 35

oxidation state of +5. Therefore, it can only decrease its O.N. and hence, it acts as an oxidising agent only.

(c) A reaction in which a particular species simultaneously gets oxidised and reduced, is known as disproportionation reaction.

$$e.g.$$
,  $Hg_2Cl_2 \longrightarrow Hg + HgCl_2$ 

In this reaction, Hg<sub>2</sub>Cl<sub>2</sub> is getting oxidised to HgCl<sub>2</sub> and also getting reduced to Hg.

OR

(a) As oxidation numbers are not changing of any element hence, the given reaction is not a redox reaction.

(b) The given reaction is a redox reaction. Oxidant/oxidising agent : HCl.

Reductant/reducing agent : Zn

The given reaction is a redox reaction. Oxidant/oxidising agent : BrO<sub>3</sub> Reductant/reducing agent: Fe<sup>2+</sup>

The given reaction is a redox reaction. Oxidant/oxidising agent : O<sub>2</sub> Reductant/reducing agent : Zn

The given reaction is a redox reaction. Oxidant/oxidising agent : IO<sub>4</sub> Reductant/reducing agent: Sn<sup>2+</sup>

35.			
	Condensed formula	<b>Bond-line formula</b>	Functional group
(a)	CH <sub>3</sub> $\mid$ CH <sub>3</sub> —C—CH <sub>2</sub> —CH—CH <sub>3</sub> $\mid$ $\mid$ CH <sub>3</sub> $\mid$ CH <sub>3</sub> $\mid$ CH <sub>3</sub> 2, 2, 4-Trimethylpentane	$2 \downarrow 4 \downarrow 5$	No functional group, single bonds
(b)	CH <sub>2</sub> COOH  HO—C—COOH  CH <sub>2</sub> COOH  2-Hydroxy-1, 2, 3-propanetricarboxylic acid	о соон о но он	O    -C-OH, -OH Carboxylic acid Alcohol
(c)	CH=CH $H_2C$ $CH_2$ $H_2C$ $CH_2$ $CH=CH$ $Cycloocta-1, 5-diene$	$ \begin{array}{c} 1 & 2 \\ 8 & 7 & 4 \end{array} $	Double bonds
(d)	$\begin{array}{c} \text{O} \\ \text{H} \\ \text{C} \\ \text{CH}_2 $	$H \xrightarrow{0} \xrightarrow{3} \xrightarrow{5} \xrightarrow{6} H$	O    —C—H Aldehyde
(e)	CH <sub>3</sub> —CH—COOH  CH <sub>3</sub> —C—CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> 2-(4-iso-butylphenyl) Propanoic acid	ОН	O    COH Carboxylic acid

## ELECTROCHEMISTRY | CHEMICAL KINETICS

#### ELECTROCHEMISTRY

#### Electrochemical cell or Galvanic cell convert chemical energy to electrical energy

#### CELL

#### (Device to convert chemical energy to electrical energy or vice-versa)

#### Electrolytic cell convert electrical energy to chemical energy

Flow of current is opposite to the flow of electrons.

Conductance of electricity through electrolytic solution.  $R = \frac{\rho l}{A}$ ;  $G = \frac{1}{R}$ ;  $\kappa = \frac{1}{\rho} = \frac{l}{RA}$ 

Electrode Potential: It is defined as the tendency of an electrode to either lose or gain electrons.

Measurement of conductivity of ionic solution using conductivity cell.

Cell constant  $(G^*)$ :  $G^* = \frac{l}{A} = R\kappa$ , So,  $\kappa = \frac{\text{Cell constant}}{R}$ 

Cell Potential: The difference between electrode potentials of two half cells is called cell potential or cell voltage or electromotive force (EMF) of the cell.

Molar Conductivity  $(\Lambda_m)$ :  $\Lambda_m = \frac{\kappa}{C} \times 1000$ 

EMF of cell :  $E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ (in terms of standard reduction electrode potential).

Variation of conductivity with concentration: Conductivity decreases with decrease in concentration for both weak and strong electrolyte.

#### **Nernst Equation and Electrochemical Series**

**Nernst equation**: For the reaction:

$$M^{n+} + ne^- \rightarrow M$$
,  $E = E^\circ - \frac{RT}{nF} \ln \frac{M}{[M^{n+}]}$  or

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$
 at 298 K

$$E_{\text{cell}}^{\text{o}} = \frac{2.303 \, RT}{nF} \log K \text{ (at equilibrium, } E_{\text{cell}} = 0)$$

$$\Delta G^{\text{o}} = -nFE_{\text{cell}}^{\text{o}}, \Delta G^{\text{o}} = -RT \ln K$$

Electrochemical series: Elements arranged in increasing or decreasing order of their standard electrode potential.  $F_2 > Co^{3+} > Ag^+ > Cu^{2+} > Cr^{3+} > K^+ > Li^+$ 

Decreasing order of reduction electrode potential.

Decreasing order of oxidising power.

#### Uses: Electrochemical cells are extensively used for determining the pH of solution, solubility product, equilibrium constant and for potentiometric titrations.

#### Variation of molar conductivity

For a strong electrolyte: On dilution, there is only small increase in conductance.

For a weak electrolyte: On dilution, there is large increase in conductance especially near infinite dilution.

Limiting molar conductivity ( $\Lambda_m^{\circ}$ ): When concentration approaches zero.

Kohlrausch's law of independent migration:

$$M_x N_y \longrightarrow x M^{y+} + y N^{x-}; \ \Lambda_m^{\circ} = x \lambda_M y^+ + y \lambda_N x^-$$

For weak electrolyte:  $\alpha = \frac{\Lambda_m}{\alpha}$ 

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C\Lambda_m^2}{\Lambda_m(\Lambda_m - \Lambda_m)}$$

**Electrolysis:** Faraday 1<sup>st</sup> law of electrolysis:  $w \propto \theta$ ;  $w \propto It$ ; w = ZIt

(w = weight of substance deposited/discharged at any)electrode, Z = electrochemical equivalent.)

 $2^{\text{nd}}$  Law of electrolysis:  $\frac{w_I}{w_{II}} = \frac{\text{Eq. } wt_1}{\text{Eq. } wt_2}$ 

#### **Commercial Cells (Batteries)**

Two or more galvanic cells connected in series is called battery. They are mainly primary batteries, secondary batteries and fuel cells.

#### CHEMICAL KINETICS

#### **Rate of Reaction**

It is defined as the change in concentration of any one of the reactant or product in unit time.

#### **Important Relations:**

For a reaction,  $aA + bB \rightarrow xX + yY$ 

Rate of reaction = 
$$-\frac{1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = +\frac{1}{x}\frac{d[X]}{dt} = +\frac{1}{y}\frac{d[Y]}{dt}$$

But, rate of disappearance of  $A = -\frac{d[A]}{dA} = a \times \text{Rate of}$ reaction

Rate of formation of  $X = +\frac{d[X]}{dX} = n \times Rate$  of reaction

#### Factors Affecting the Rate of a Reaction

- Concentration of reactants
- Presence of light
- Catalyst
- Surface area
- Temperature
- Rate law expression :  $aA + bB \longrightarrow cC + dD$

Rate  $\propto [A]^x[B]^y$ , x and y are different from 'a' and 'b'

 $R = k[A]^x [B]^y$ 

k = Rate constant

Order of reaction = x + y

Rate law cannot be decided by the chemical reaction and can be calculated experimentally.

	1 /				
Order	Molecularity				
• Experimentally determined.	Theoretically calculated.				
• Can be zero and even	<ul> <li>Cannot be zero or</li> </ul>				
a fraction.	integer.				
<ul> <li>Applicable to</li> </ul>	<ul> <li>Molecularity has no</li> </ul>				
elementary as well as	meaning for complex				
complex reaction.	reaction.				

Rate constant: It is equal to the rate of reaction when the concentration of each of the reactants is unity. Units of rate constant (k) for an  $n^{th}$  order reaction :  $k = (\text{conc.})^{1-n} \text{ time}^{-1}$ 

Pseudo first order reaction: Change in concentration of one of the reactant is negligible, e.g.,

- Hydrolysis of ester
- Hydrolysis of sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

 $R = k[C_{12}H_{22}O_{11}][H_2O]$ {[H<sub>2</sub>O] is negligible.}  $k \cdot [H_2O] = K^*; R = k^*[C_{12}H_{22}OH_{11}]$ 

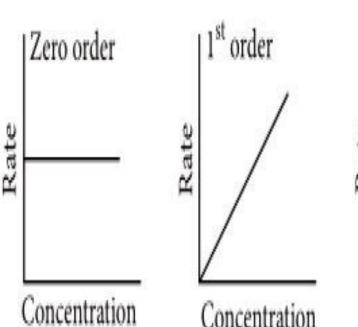
#### Integrated Rate Law

For zero order: 
$$k = \frac{1}{t} \{ [A]_0 - [A] \}$$
;  $t_{1/2} = \frac{[A]_0}{2k_0}$ 

For first order: 
$$k = \frac{2.303}{t} \log \left( \frac{a}{a - x} \right)$$
;  $t_{1/2} = \frac{0.693}{k_1}$ 

#### Some Important Graphs of Different order of Reactions

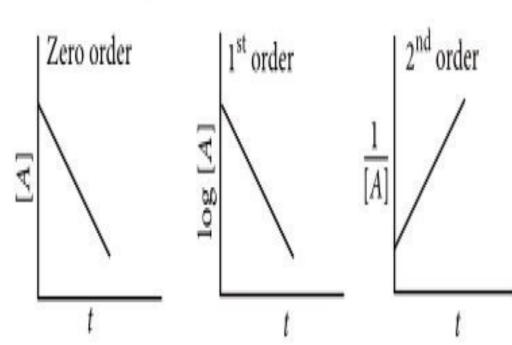
• Plots of rate vs concentration



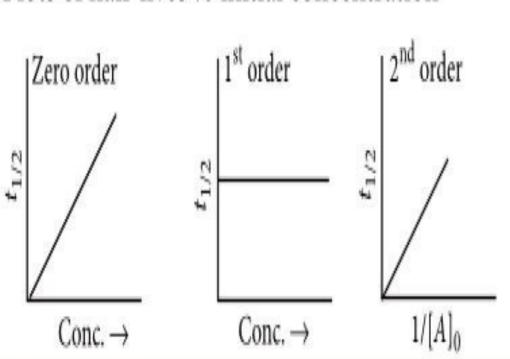
(Concentration)

2<sup>nd</sup> order

Plots of integrated rate equations



• Plots of half-lives *vs* initial concentration



#### Temperature Dependence on the Rate of a Reaction

**Collision theory:**  $k = PZe^{-E_a/RT}$ where, P = steric factor, Z = collision frequency Effective collision: Collision with sufficient kinetic energy and proper orientation.

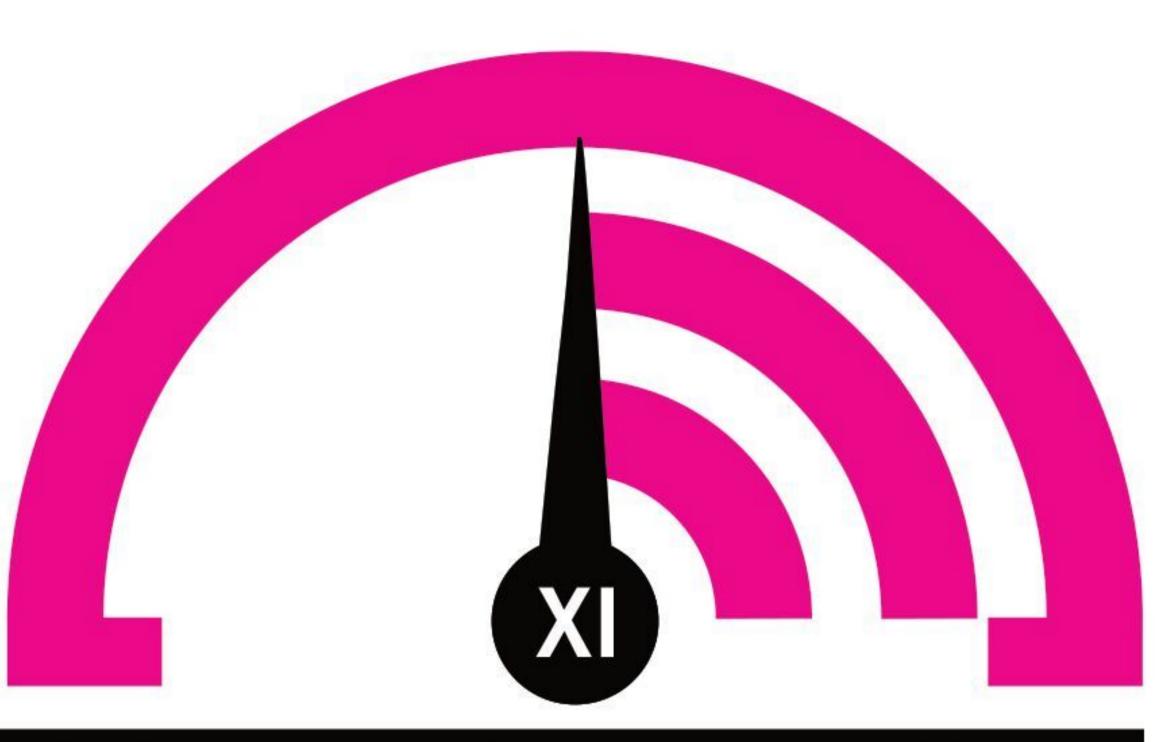
**Arrhenius equation**: Arrhenius proposed a quantitative relation-Slope =  $\frac{-E_a}{R}$ ship between rate constant and lnk temperature as  $k = Ae^{-E_a/RT}$  $\ln k = \ln A - \frac{E_a}{RT}$ ;  $\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$ 

 $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$ 

Catalyst: Provide alternate path with lower activation energy.

- Does not alter Gibb's energy.
- Does not change equilibrium constant.

# MONTHLY TEST D R I V E



his specially designed column enables students to self analyse their extent of understanding the specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks: 120 Organic Chemistry - Some Basic Principles and Techniques Time Taken: 60 Min.

#### NEET

#### **Only One Option Correct Type**

1. The IUPAC name of the compound

- (a) 5-formylhex-2-en-3-one
- (b) 5-methyl-4-oxohex-2-en-5-al
- (c) 3-keto-2-methylhex-5-enal
- (d) 3-keto-2-methylhex-4-enal
- 2. The order of decreasing stability of the following carbanions is
  - (i)  $(CH_3)_3C^{-1}$
- (ii)  $(CH_3)_2CH^-$
- (iii)  $CH_3CH_2^-$
- (iv)  $C_6H_5CH_2$
- (a) (i) > (ii) > (iv)
- (b) (iv) > (iii) > (ii) > (i)
- (c) (iv) > (i) > (ii) > (iii)
- (d) (iii) > (ii) > (iv)
- 3. How many primary, secondary, tertiary and quarternary (if any) carbon atoms are present in the following compound?

$$\begin{array}{c} \operatorname{CH}_3 \\ \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 - \operatorname{C} - \operatorname{CH}_3 \\ \operatorname{CH}_3 & \operatorname{CH}_3 \\ \end{array}$$

- (a) One primary, two secondary and one tertiary
- (b) Five primary and three secondary
- (c) Five primary, one secondary, one tertiary and one quarternary
- (d) Four primary, two secondary and two quarternary.

4. Which carbocation is the least stable?

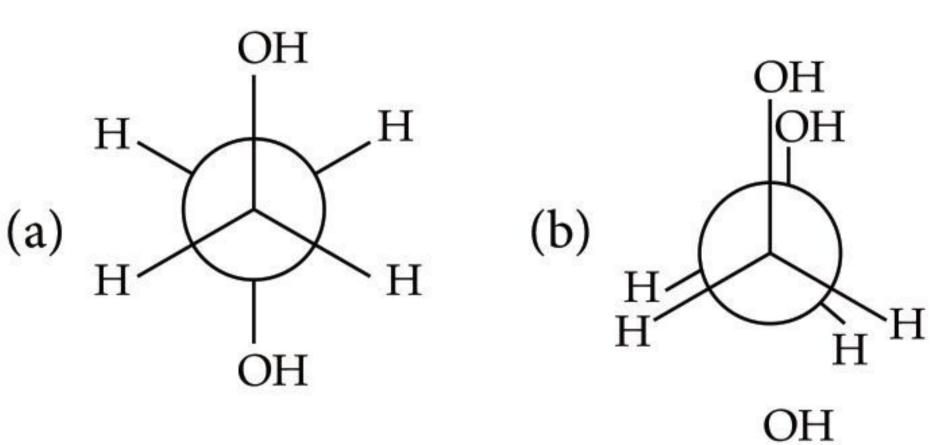
(a) 
$$\stackrel{\stackrel{+}{\leftarrow}}{\bigcap}$$
 (b)  $\stackrel{\stackrel{+}{\leftarrow}}{\bigcap}$  (c)  $\stackrel{\stackrel{+}{\leftarrow}}{\bigcap}$  (d)  $\stackrel{\stackrel{+}{\leftarrow}}{\bigcap}$  NO<sub>2</sub>

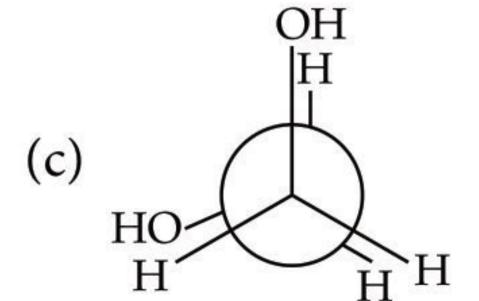
5. Which type of intermediate (*A*) is formed during the reaction?

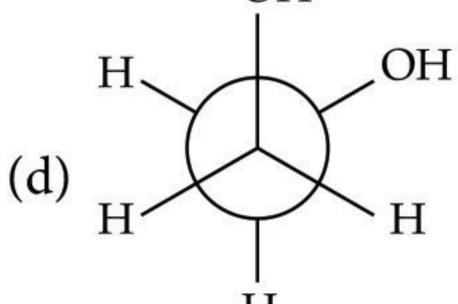
$$CH_3CH_2 - N = N - CH_2CH_3 \xrightarrow{Heat} (A) + N_2$$

- (a) Carbocation
- (b) Carbanion
- (c) Free radical
- (d) Carbene
- 6. Correct representation of 3-methylpent-3-en-2-ol is

7. Which of the following conformers for ethylene glycol is most stable?







- 0.765 g of an acid gives 0.535 g of CO<sub>2</sub> and 0.138 g of H<sub>2</sub>O. Then the ratio of the percentage of carbon and hydrogen is
  - (a) 19:2 (b) 18:11 (c) 70:17 (d) 1:7
- Which of the following pairs of compounds does not represent structural isomers?

- 10. Which of the following is a false statement?
  - (a) Free radicals, carbonium ions and carbanions are reaction intermediates.
  - (b) Reaction between methane and chlorine in presence of sunlight proceeds via free radical.
  - (c) The electronegative atom in the carbon chain produces +I effect.
  - (d) Homolytic fission of C-C bonds gives free radicals.
- 11. Which of the following carbocations is expected to be most stable?

(a) 
$$\stackrel{NO_2}{\downarrow}$$
 (b)  $\stackrel{NO_2}{\downarrow}$  (c)  $\stackrel{NO_2}{\downarrow}$  (d)  $\stackrel{NO_2}{\downarrow}$ 

12. Which of the following biphenyls is optically active?

(a) 
$$O_2N$$
(b)  $O_2N$ 
(c)  $O_2N$ 
(d)  $O_2N$ 
 $O_2N$ 

#### Assertion & Reason Type

**Directions**: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.
- 13. Assertion: Alkanes containing more than three carbon atoms exhibit chain isomerism.

Reason: In an alkane, all carbon atoms are sp<sup>3</sup> hybridised.

14. Assertion: The order of reactivity of carbocation is  $2^{\circ} > 3^{\circ} > 1^{\circ}$ .

**Reason**: Carbon atom in carbonium ion is in sp<sup>3</sup> state of hybridisation.

15. Assertion: When inductive and electromeric effects operate in opposite directions, the inductive effect predominates.

Reason: Inductive effect is the complete transfer of shared pair of  $\pi$  electrons to one of the atoms.

#### **JEE MAIN / JEE ADVANCED**

#### Only One Option Correct Type

- 16. The number of structural and configurational isomers of a bromo compound, C<sub>5</sub>H<sub>9</sub>Br, formed by the addition of HBr to 2-pentyne respectively are
  - (a) 1 and 2
- (b) 2 and 4
- (c) 4 and 2
- (d) 2 and 1
- 17. The correct stability order for the following species is

- (a) (II) > (IV) > (I) > (III)
- (b) (I) > (II) > (III) > (IV)
- (c) (II) > (I) > (IV) > (III)
- (d) (I) > (III) > (IV)
- 18. Amongst the following which are true for  $S_N 2$ reaction?
  - The rate of reaction is independent of the concentration of the nucleophile.
  - (ii) The nucleophile attacks the carbon atom on the side of the molecule opposite to the group being displaced.
  - (iii) The reaction proceeds with simultaneous bond formation and bond rupture.

- (a) (i) and (ii) (b) (i) and (iii)
- (c) (i), (ii) and (iii) (d) (ii) and (iii)
- 19. A dibasic acid containing C, H and O was found to contain C = 26.7% and H = 2.2%. The vapour density of diethyl ester was found to be 73. What is the molecular formula of acid?
  - (a)  $CH_2O_2$
- (b)  $C_2H_2O_4$
- (c)  $C_3H_3O_4$
- (d)  $C_4H_4O_4$

#### More than One Option Correct Type

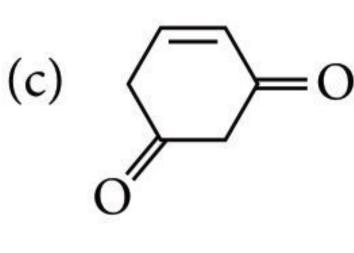
- 20. Which of the following compounds will show geometrical isomerism?
  - (a) 2-Butene
- (b) Propene
- (c) 1-Phenyl propene (d) 2-Methyl butene
- 21. Which of the following compounds have asymmetric C-atom?

(a) 
$$CH_3-CH_2-CH_2$$
 (b)  $CH_3-CH-CH-CH_3$  Br  $CH_3$ 

- 22. In the Newman projection for 2, 2-dimethylbutane, X and Y can respectively be
  - (a) H and H
  - (b) H and  $C_2H_5$
  - (c)  $C_2H_5$  and H
  - (d) CH<sub>3</sub> and CH<sub>3</sub>
- 23. Tautomerism is exhibited by

=0

(b) 
$$O = \bigcirc O$$
(d)  $\bigcirc O$ 



Η

#### Integer / Numerical Value Type

- 24. How many isomers are possible for the compound having molecular formula C<sub>3</sub>H<sub>5</sub>Br<sub>3</sub>?
- 25. 0.50 g of an organic compound was Kjeldahlised and the NH<sub>3</sub> evolved was absorbed in 50 mL of

- 0.5 M H<sub>2</sub>SO<sub>4</sub>. The residual acid required 60 cm<sup>3</sup> of 0.5 M NaOH. The percentage of nitrogen in the organic compound is \_\_\_\_\_.
- 26. Out of the following reagents, electrophiles
  - (i)  $R_3N$
- (ii) :CCl<sub>2</sub>
- (iii) CH<sub>3</sub><sup>+</sup>
- (iv)  $H_2O$
- (v)  $H_3O^+$
- (vi) NH<sub>3</sub>

#### **Comprehension Type**

Stability of carbocation, alkyl free radical and alkene can be explained on the basis of hyperconjugation. In all these cases, there is presence of hydrogen atom at the adjacent carbon atom of  $sp^2$  hybridised carbon. Total number of hyperconjugating structures depends upon the number of hydrogen atoms present at adjacent carbon atom of  $sp^2$  carbon. More the hyperconjugating structures, more is the stability of the ion.

- 27. Hyperconjugation is not possible in
  - (a)  $CH_3 CH = CH_2$  (b)  $CH_2 = CH_2$

(c) 
$$CH_3 - \overset{+}{C} < \overset{CH_3}{CH_3}$$
 (d)  $CH_3 - C = C - CH_3$   $CH_3 - CH_3 = C + CH_3$ 

- 28. Decreasing order of stability of following alkenes is
  - (i)  $CH_3 CH = CH_2$  (ii)  $CH_3 CH = CH CH_3$

(iii) 
$$CH_3 - C = CH - CH_3$$
 (iv)  $CH_3 - C = C - CH_3$   $CH_3$   $CH_3$ 

- (a) (i) > (ii) > (iii) > (iv)
- (b) (iv) > (iii) > (ii) > (i)
- (c) (iii) > (ii) > (iv)
- (d) (ii) > (iii) > (iv) > (i)

#### **Matching Type**

29. Match the reactions in column I with their types given in column II and select the correct option.

	Column I		Column II		
(A)	Inductive	(i)	Delocalisation of σ		
	effect		electrons through the		
			overlapping of <i>p</i> -orbital.		
(B)	Resonance	(ii)	Strong effect		
(C)	No bond resonance	(iii)	Permanent effect		
(D)	Electromeric effect	(iv)	Delocalisation of $\pi$ electrons		

(a) 
$$(A) \rightarrow (i)$$
,  $(B) \rightarrow (iv)$ ,  $(C) \rightarrow (iii)$ ,  $(D) \rightarrow (ii)$ 

(b) (A) 
$$\rightarrow$$
 (iv), (B)  $\rightarrow$  (iii), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (ii)

(c) 
$$(A) \to (iii), (B) \to (iv), (C) \to (i), (D) \to (ii)$$

(d) (A) 
$$\rightarrow$$
 (i), (B)  $\rightarrow$  (iii), (C)  $\rightarrow$  (iv), (D)  $\rightarrow$  (ii)

30. Match the column I (organic compounds) with column II (their IUPAC names) and select the correct option.

	Column I		Column II
(A)	>< \OH	(i)	3,7-Dimethylocta-
			1,3,6-triene
(B)	OH OH	(ii)	4-Methyl-5- oxohexanoic acid

(C)	$\bigvee_{O}$ OH	(iii)	3,3,5-Trimethylhex- 1-en-2-ol
(D)		(iv)	4-Hydroxy-4- methylpentan-2- one

(a) 
$$(A) \rightarrow (ii), (B) \rightarrow (i), (C) \rightarrow (iii), (D) \rightarrow (iv)$$

(b) 
$$(A) \rightarrow (iv), (B) \rightarrow (ii), (C) \rightarrow (i), (D) \rightarrow (iii)$$

(c) 
$$(A) \rightarrow (i), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (iv)$$

(d) (A) 
$$\rightarrow$$
 (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (ii), (D)  $\rightarrow$  (i)



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Marks scored in percentage < 60% NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

Unscramble the words given in column I and match them with their explanations in column II.

#### Column I

#### 1. LATOCCUIONLF

- 2. ALLLBEEAM
- 3. DOOLLIC
- YLPSISROY
- 5. TORLASUIN
- LISEMUREIF
- **TONRISPO**
- 8. REEUAS
- 9. TYLIAROM
- 10. SAOBERMUGI

#### Column II

- A heterogeneous system in which one substance is dispersed as very fine particles in another substance called dispersion medium.
- Stabilising agent that prevents immiscible liquids from separating.
- The process by which the dispersed particles in a colloid come out of suspension to aggregate into larger clumps.
- Any material that resists the flow of electric current.
- A measure of the concentration of a chemical species, especially of a solute in a solution.
- Able to be shaped or pounded with a hammer, usually applied to metals.
- The antimatter counterpart of an electron, which has a charge of +1. (g)
- Radioactive transition metal with element symbol Sg. (h)
- The thermal decomposition of materials at elevated temperature in an (i) inert atmosphere such as a vacuum gas.
- Nickle-dependent enzyme which catalyses the hydrolysis of urea to ammonia and CO<sub>2</sub>.

Readers can send their responses at editor@mtg.in or post us with complete address by 10<sup>th</sup> of every month. Winners' names will be published in next issue.

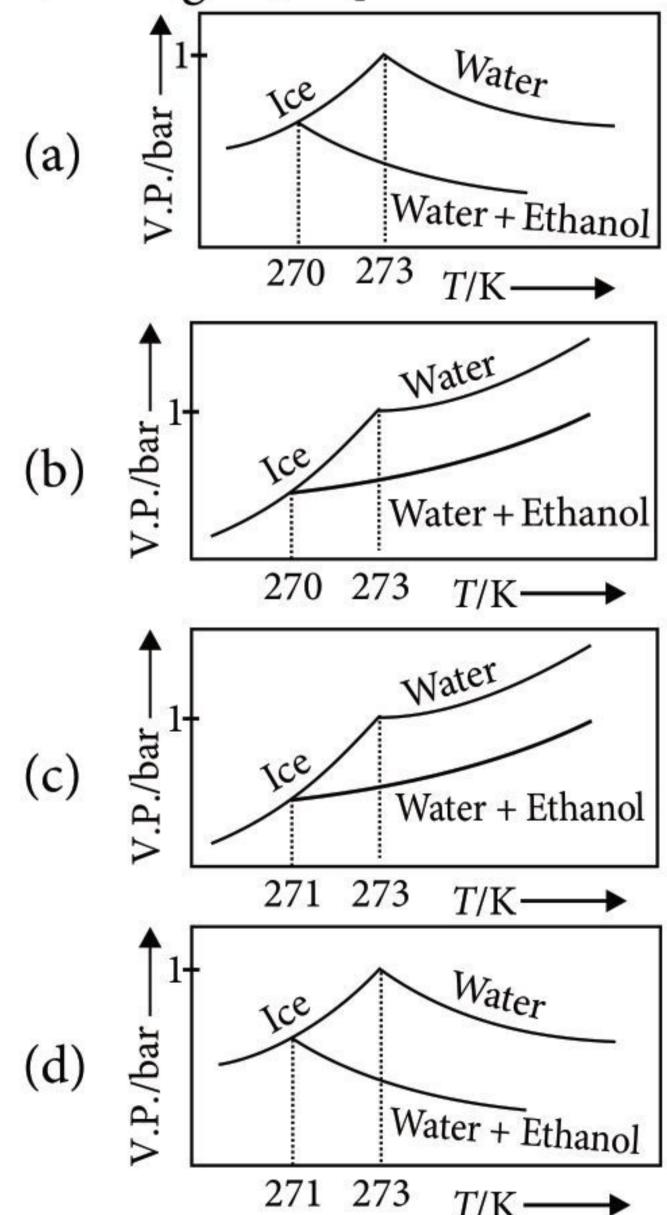
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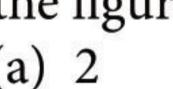
Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T).

Among the following, the option representing change in the freezing point is

[Given: Molecular weight of ethanol is 46 g mol<sup>-1</sup> and the freezing point depression constant of water is  $2 \text{ K kg mol}^{-1}$ .



In the reaction,  $P + Q \rightarrow R + S$ , the time taken for 75% [Q]<sub>0</sub> reaction of *P* is twice the time taken for 50% reaction of P. [Q] The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is



- (a) 2 (b) 3 (c) 0 (d) 1

Time

- Identify the incorrect statement. 3.
  - The S S –S bond angles in the  $S_8$  and  $S_6$  rings are the same.
  - Rhombic and monoclinic sulphur have S<sub>8</sub> molecules.
  - S<sub>2</sub> is paramagnetic like oxygen.
  - (d) S<sub>8</sub> molecule has a crown shape.
- Match the List I with List II and select the correct option.

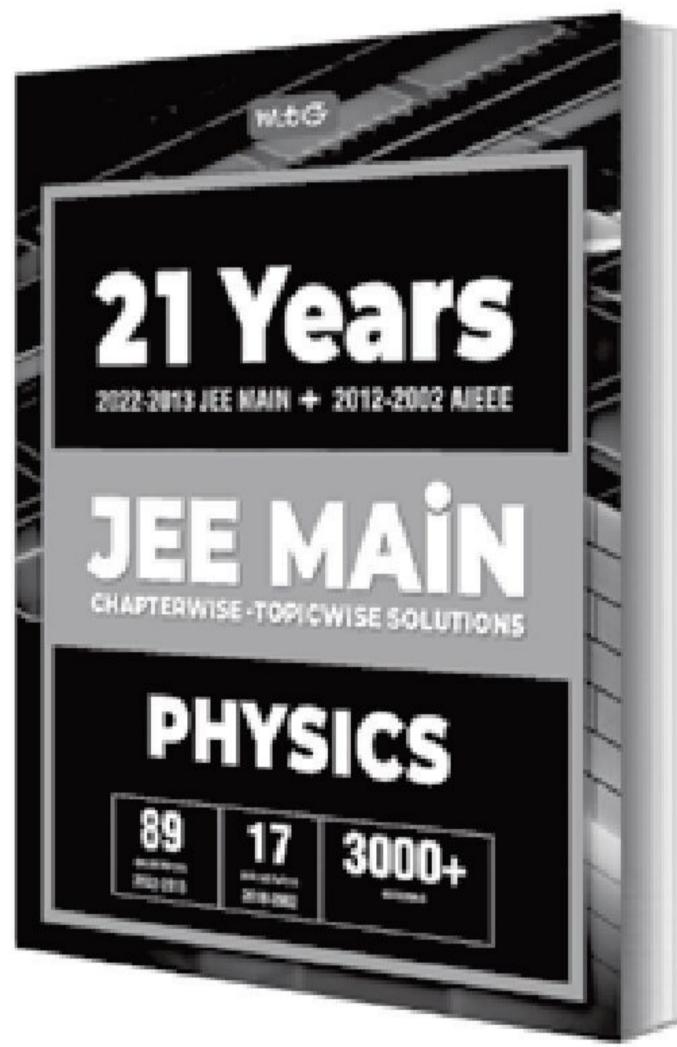
	List I		List II		
(A)	$[Ag(CN)_2]^-$	(i)	Square planar and 1.73 B.M.		
4 22 24		Parties No.			
(B)	$[Cu(CN)_4]^{3-}$	(ii)	Linear and 0 B.M.		
(C)	$[Cu(CN)_6]^{4-}$	(iii)	Octahedral and 0 B.M.		
(D)	$[Cu(NH_3)_4]^{2+}$	(iv)	Tetrahedral and zero		
(E)	$[Fe(CN)_6]^{4-}$	(v)	Octahedral and 1.73 B.M.		

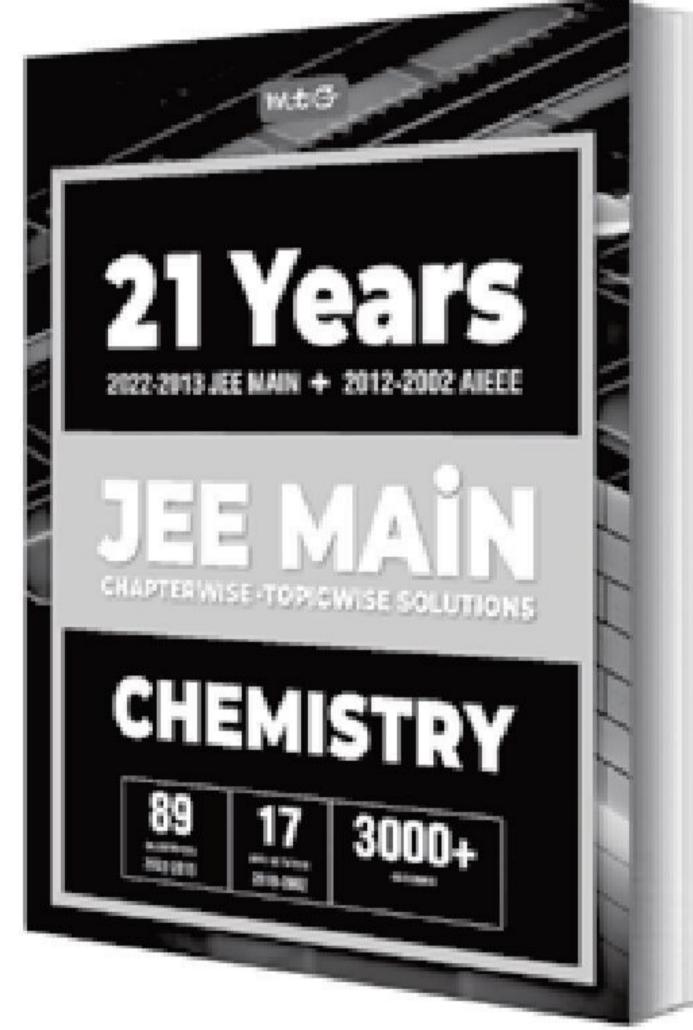
- (a) A (ii), B (iv), C (v), D (i), E (iii)
- (b) A (v), B (iv), C (i), D (iii), E (ii)

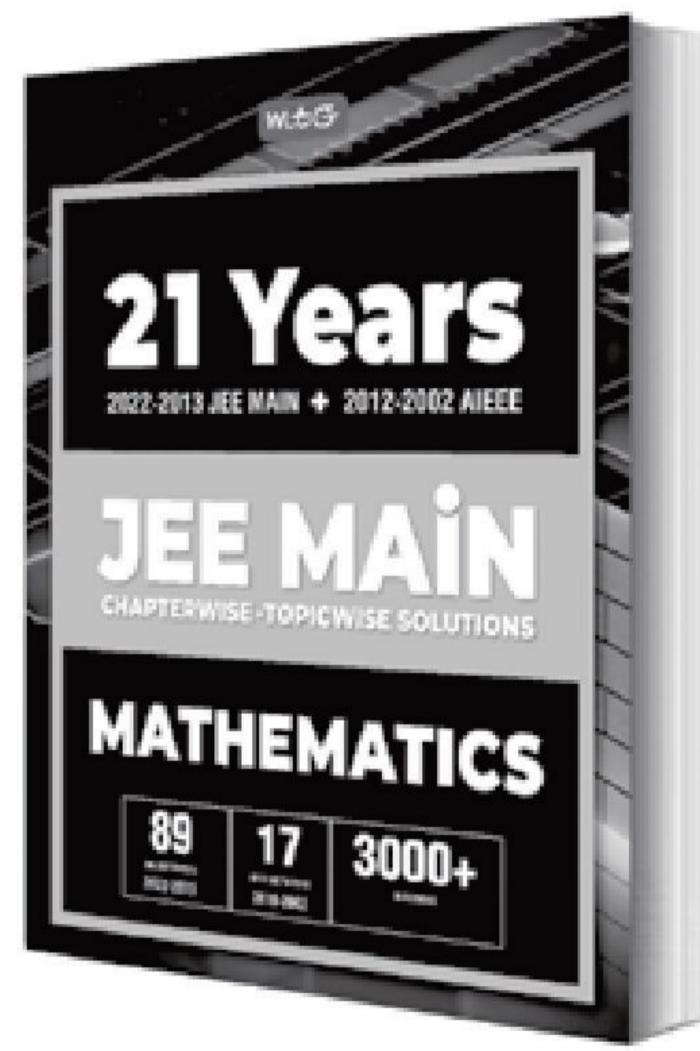


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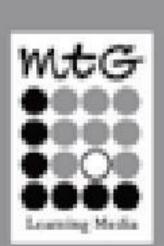
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- (c) A (i), B (iii), C (iv), D (ii), E (v)
- (d) A (iv), B (v), C (ii), D (i), E (iii)
- Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest  $E_{M^{3+}/M^{2+}}^{o}$  value?
  - (a) Co (Z = 27)
- (b) Cr(Z = 24)
- (c) Mn (Z = 25) (d) Fe (Z = 26)
- Na and Mg crystallize in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
  - 4 and 2 (a)
- (b) 9 and 14
- 14 and 9
- (d) 2 and 4
- Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations.

$$CH_3-CH_2-CH_2Br \xrightarrow{X} Product \xrightarrow{Y}$$

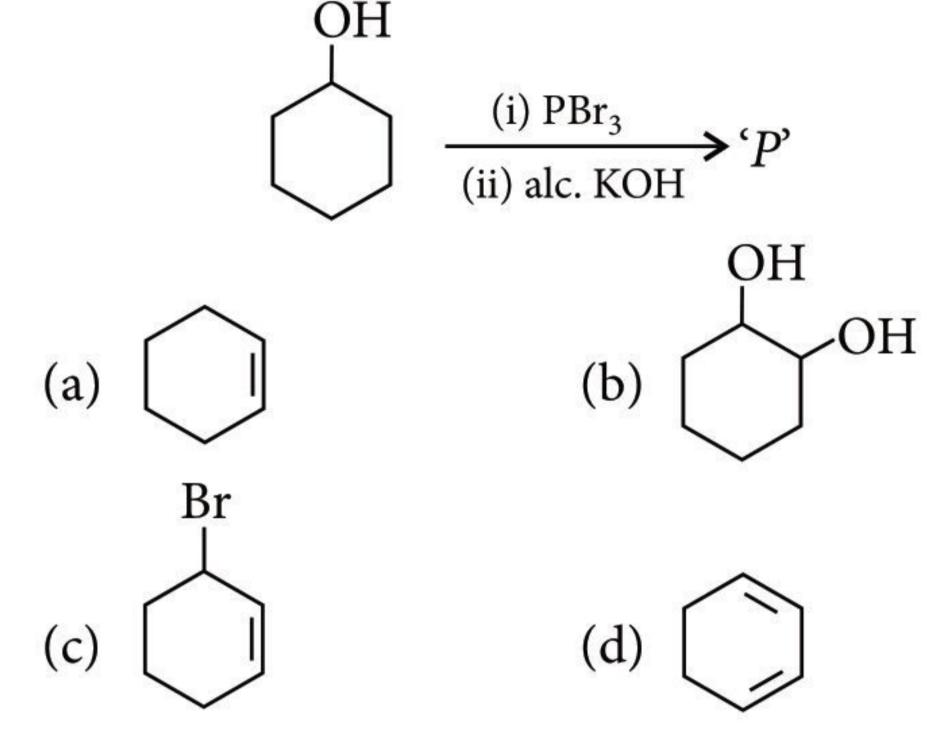
$$CH_3-CH-CH_3$$

$$Rr$$

- X = Dilute aqueous NaOH, 20°C;Y = HBr/acetic acid 20°C
- $X = \text{Concentrated alcoholic NaOH, } 80^{\circ}\text{C};$ Y = HBr/acetic acid 20°C
- X = Dilute aqueous NaOH, 20°C; $Y = Br_2/CHCl_3$ , 0°C
- $X = \text{Concentrated alcoholic NaOH, } 80^{\circ}\text{C};$  $Y = Br_2/CHCl_3$ , 0°C.
- An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct option.

	List I		List II
(P)	$(C_2H_5)_3N + CH_3COOH$	(i)	Conductivity
	(X) $(Y)$		decreases and then
			increases.
(Q)	$KI(0.1M) + AgNO_3(0.01 M)$	(ii)	Conductivity
	(X) $(Y)$		decreases and then
			does not change
			much.
(R)	$CH_3COOH + KOH$	(iii)	Conductivity
	(X) $(Y)$		increases and then
			does not change
			much.
(S)	NaOH + HI	(iv)	Conductivity does
	(X) $(Y)$		not change much
			and then increases.

- (a) (P) (iii), (Q) (iv), (R) (ii), (S) (i)
- (b) (P) (iv), (Q) (iii), (R) (ii), (S) (i)
- (c) (P) (ii), (Q) (iii), (R) (iv), (S) (i)
- (d) (P) (i), (Q) (iv), (R) (iii), (S) (ii)
- Predict the final product 'P'.



- 10. In Cannizzaro reaction given below:  $2PhCHO \xrightarrow{OH^-} PhCH_2OH + PhCOO^$ the slowest step is
  - the attack of OH<sup>-</sup> at the carboxyl group
  - the transfer of hydride to the carbonyl group
  - the abstraction of proton from the carboxylic group
  - the deprotonation of PhCH<sub>2</sub>OH.
- 11. The action of nitrous acid on an aliphatic primary amine gives
  - secondary amine
- nitroalkane (b)
- (c) alcohol
- (d) alkyl nitrite.
- Polydispersity index (PDI) is
- (c)  $\bar{M}_{n} \times \bar{M}_{w}$

#### **NUMERICAL PROBLEMS**

13. Among the following, how many compounds show the behaviour of neutral flux? KF, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>3</sub>AlF<sub>6</sub>, MgSiO<sub>3</sub>, CaF<sub>2</sub>, NaF, Mn<sub>3</sub>O<sub>4</sub>

14. The number of chiral carbon(s) present in peptide,

Ile-Arg-Pro, is \_\_\_\_\_.

15. The number of  $sp^2$ -hybridised carbons present in "Aspartame" is \_\_\_\_\_.

#### **SOLUTIONS**

(b): Depression in freezing point,  $\Delta T_f = K_f \cdot m$ where,  $K_f$  = Freezing point depression constant, m = Molality

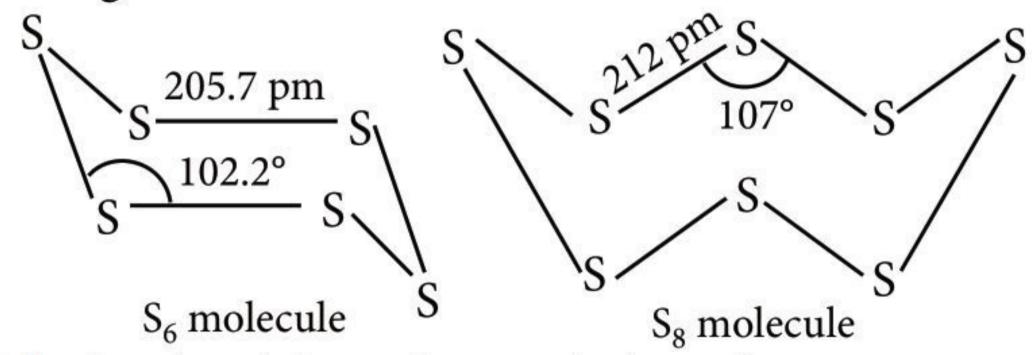
$$m = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (in kg)}} = \frac{\frac{34.5}{46}}{\frac{500}{1000}} = 1.5 \text{ mol kg}^{-1}$$

.. 
$$\Delta T_f = 2 \times 1.5 = 3 \text{ K}$$
  
 $\Delta T_f = T_f^{\circ} - T_f$   
 $3 = 273 - T_f$  (Freezing point of H<sub>2</sub>O = 273 K)  
 $T_f = 273 - 3 = 270 \text{ K}$ 

Thus, freezing point of solution = 270 K

Also, as temperature increases, the vapour pressure increases. Hence, the correct curve is given in option (b).

- 2. (d): For P, if  $t_{50\%} = x$ , then  $t_{75\%} = 2x$ . So, order with respect to P is 1. From the given graph, concentration of Q decreases linearly with time. So, rate with respect to Q, remains constant. Hence, order of reaction with respect to Q is zero. The rate law expression;  $r = k[P]^1[Q]^0$  So, overall order is 1 + 0 = 1.
- 3. (a): Sulphur has puckered  $S_8$  rings with crown conformation and Engel's sulphur contains  $S_6$  rings arranged in a chair conformation.



4. (a):  $[Ag(CN)_2]^-$  is linear (sp) with no unpaired electron hence, magnetic moment = 0  $[Cu(CN)_4]^{3-}$  is tetrahedral  $(sp^3)$  with no unpaired electron hence, magnetic moment = 0

 $[Cu(CN)_6]^{4-}$  is octahedral  $(sp^3d^2)$  with one unpaired electron hence, magnetic moment  $= \sqrt{1(1+2)} = 1.73 \text{ B.M.}$ 

 $[Cu(NH_3)_4]^{2+}$  is square planar  $(dsp^2)$  with one unpaired electron hence, magnetic moment  $=\sqrt{1(1+2)}=1.73$  B.M.

 $[Fe(CN)_6]^{4-}$  is octahedral  $(d^2sp^3)$  with no unpaired electron hence, magnetic moment = 0.

7. **(b)**: 
$$CH_3 - CH_2 - CH_2Br$$
  $\frac{NaOH (alc.)}{80^{\circ}C, -HBr}$ 

$$CH_3 - CH - CH_3 \leftarrow \frac{HBr}{CH_3} CH_3 - CH = CH_2$$

$$Rr$$

8. (a):  

$$P: (C_2H_5)_3N + CH_3COOH \longrightarrow$$
  
(X) (Y)  $CH_3COO^- + (C_2H_5)_3NH^+$ 

Initially, conductivity increases due to ion formation after that, it becomes practically constant because *X* alone cannot form ions.

$$Q: KI(0.1 M) + AgNO_3(0.01 M) \longrightarrow AgI \downarrow + KNO_3$$
(Y)

Number of ions in the solution remains constant until all the AgNO<sub>3</sub> is precipitated out as AgI. Thereafter, conductance increases due to increase in number of ions.

$$R: CH_3COOH + KOH \longrightarrow CH_3COOK + H_2O$$
(X) (Y)

Initially, conductance decreases due to the decrease in the number of OH<sup>-</sup> ions. Thereafter, it slowly increases (not much) due to increase in number of H<sup>+</sup> ions as CH<sub>3</sub>COOH is a weak acid.

$$S: NaOH + HI \longrightarrow NaI + H_2O$$
(X) (Y)

Initially, conductivity decreases due to the decrease in  $H^+$  ions and then, increases due to the increase in  $OH^-$  ions.

9. (a): 
$$PBr_3$$
  $Alc.$   $ROH$   $ROH$ 

- 13. (3): The neutral compound added to decrease the melting point and to make the ore conducting in an electrolytic cell is called neutral flux, *i.e.*, CaF<sub>2</sub>, Na<sub>3</sub>AlF<sub>6</sub>, KF.
- 14. (4):

$$\begin{array}{c} \text{NH}_2 \\ \text{NH-C=NH} \\ \text{O} \quad (\text{CH}_2)_3 \text{O} \quad \text{COOH} \\ \text{NH}_2-\overset{*}{\text{CH}}-\text{C-NH-}\overset{*}{\text{CH}}-\text{C-N} \\ \overset{*}{\text{-}} \\ \text{CH}_2-\text{CH}_3 \\ \text{CH}_3 \quad \text{Ile-Arg-Pro} \end{array}$$

15. (9):

HO—
$$C$$
— $CH_2$ — $CH$ — $C$ — $NH$ — $CH$ — $C$ — $OCH_3$ 

$$NH_2 \qquad CH_2$$
(Aspartame)

Total number of  $sp^2$  hybridised carbon atoms is 9.



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Unit 4

#### The p-Block Elements | The d- and f-Block Elements

#### The *p*-Block Elements

#### GROUP 15 ELEMENTS (NITROGEN FAMILY)

#### **Electronic Configuration**

Element	At. No.	Electronic Configuration	Oxidation State
Nitrogen (N)	7	[He] $2s^2 2p^3$	-3, -2, -1, 0, +1, +2, +3, +4, +5
Phosphorus (P)	15	[Ne] $3s^2 3p^3$	-3, +3, +5
Arsenic (As)	33	[Ar] $3d^{10}4s^24p^3$	-3, +3, +5
Antimony (Sb)	51	[Kr] $4d^{10}5s^25p^3$	-3, +3, +5
Bismuth (Bi)	83	[Xe] $4f^{14}5d^{10}6s^26p^3$	+3, +5
Moscovium (Mc)	115	[Rn] $5f^{14}6d^{10}7s^27p^3$	_

#### **Physical Properties**

- Atomic radii and ionic radii increase down the group and are smaller than that of group 14 elements due to increased nuclear charge.
- Melting point first increases from N to As due to increase in their atomic size and then decreases to Bi because of their tendency to form three covalent bonds instead of five due to inert pair effect.

- **Ionisation enthalpy** decreases regularly down the group due to increase in size and is much greater than group 14 elements due to extra stability of half filled *p*-orbitals.
- Electronegativity decreases down the group.
- **Allotropy**: All elements except Bi show allotropy. Phosphorus has three allotropes *i.e.*, white, red and black phosphorus. Arsenic and antimony exist in two allotropic forms *i.e.*, yellow and grey.

#### **General Trends**

- Hydrides :
  - Bond angle, Thermal stability and Basic strength: NH<sub>3</sub> > PH<sub>3</sub> > AsH<sub>3</sub> > SbH<sub>3</sub> > BiH<sub>3</sub>
  - **B.Pt.**:  $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
  - $M.Pt.: PH_3 < AsH_3 < SbH_3 < NH_3$
  - Reducing nature:
    NH<sub>3</sub> < PH<sub>3</sub> < AsH<sub>3</sub> < SbH<sub>3</sub> < BiH<sub>3</sub>
- Halides:
  - Bond angle:  $PF_3 < PCl_3 < PBr_3 < PI_3$
  - Lewis acid strength:  $PCl_3 > AsCl_3 > SbCl_3$ ;  $PF_3 > PCl_3 > PBr_3 > PI_3$

#### IMPORTANT COMPOUNDS OF NITROGEN FAMILY

Structure	Preparation	Properties	Uses
Nitrogen (N <sub>2</sub> ) N≡N	$NH_4Cl_{(aq)} + NaNO_{2(aq)} \rightarrow$ $N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$	$N_2 \xrightarrow{SNIg} Mg_3N$	In manufacturing of ammonia, used where inert atmospheres are required, in refrigerant, preservatives.

Ammonia (NH <sub>3</sub> )  N  N  H  H  H  H	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)};$ $\Delta H_f^\circ = -46.1 \text{ kJ/mol}$ (Haber's process)	$NH_{3} \xrightarrow{O_{2}} N_{2} + H_{2}O$ $\downarrow NH_{4}Cl + N_{2}$ $\downarrow If NH_{3} (excess)$ $\rightarrow NCl_{3} + HCl$ $\downarrow O_{2}, Pt \qquad If Cl_{2} (excess)$ $\rightarrow NO + H_{2}O$ $\downarrow AgCl \qquad \downarrow Ag(NH_{3})_{2}]Cl$	In refrigerators, manufacturing of rayon, HNO <sub>3</sub> (Ostwald's process), NaHCO <sub>3</sub> (Solvay's process), nitrogenous fertilizers.
Phosphine (PH <sub>3</sub> ) P P H H H H	$Ca_3P_2 + 6H_2O \longrightarrow$ $3Ca(OH)_2 + 2PH_3^{\uparrow}$		For production of smoke screens. Phosphine in combination with acetylene is used in Holme's signals.
Nitric acid (HNO <sub>3</sub> )  H\O_N \O_O O	$NaNO_3 + H_2SO_4 \xrightarrow{\Delta}$ $NaHSO_4 + HNO_3$	$HNO_{3} \xrightarrow{SO_{2} \rightarrow} H_{2}SO_{4} + NO_{2}$ $\xrightarrow{Sn \rightarrow} H_{2}SnO_{3} + NO_{2} + H_{2}O$ $\xrightarrow{HCl \rightarrow} H_{2}O + NOCl + [Cl]$	As fertilizers, explosives, perfumes, dyes and medicines. As oxidiser in rocket fuels.

#### Oxides of Nitrogen

Preparation and properties of oxides of nitrogen:

Name	Formula	O.S.	Preparation	Physical appearance and chemical nature
Dinitrogen oxide	$N_2O$	+1	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide	NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow$ $\text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	colourless gas, neutral
Dinitrogen trioxide	$N_2O_3$	+3	$2NO + N_2O_4 \xrightarrow{250 \text{ K}} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide	$NO_2$	+4	$2Pb(NO_3)_2 \xrightarrow{673 \text{ K}} 2PbO + 4NO_2 + O_2$	brown gas, acidic
Dinitrogen tetraoxide	$N_2O_4$	+4	$2NO_2 \stackrel{Cool}{\longleftarrow} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentaoxide	$N_2O_5$	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

#### **Phosphorus-Allotropic Forms**

- White phosphorus: It is a white translucent waxy solid and consists of discrete tetrahedral P<sub>4</sub> molecule.
  - It dissolves in boiling NaOH solution in an inert atmosphere giving PH<sub>3</sub> and readily catches fire.
- Red phosphorus: It is obtained by heating white phosphorus at 573 K in an inert atmosphere for several days. It possesses iron grey lustre.
- Black phosphorus: It has two forms:
  - α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.
  - β-black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

#### **Phosphine**

**Preparation:** 

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
  
 $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$ 

Properties: It is a colourless gas with rotten fish smell and is highly poisonous.

$$\begin{array}{ccccc} 4PH_3 & \xrightarrow{\Delta} & P_4 & + 6H_2 \\ & \text{Red phosphorus} \\ 3CuSO_4 + 2PH_3 & \longrightarrow & Cu_3P_2 & + 3H_2SO_4 \\ & & \text{Copper phosphide} \\ PH_3 + HBr & \longrightarrow & PH_4Br \\ & & Phosphonium bromide \\ \end{array}$$

#### **Phosphorus Halides**

Compound	Preparation	Properties	Uses
PCl <sub>5</sub> (Trigonal bipyramidal)	(white	$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ (excess) $PCl_5 + SO_2 \rightarrow SOCl_2 + POCl_3$	used as chlorinating and dehydrating agent.
PCl <sub>3</sub> (Pyramidal)	$P_4 + 6Cl_2 \rightarrow 4PCl_3$	$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$	used as reagent in organic synthesis and as a precursor.

#### **Oxoacids of Phosphorus**

Name	Formula	Oxidation state of phosphorus	Preparation
Hypophosphorous acid (Phosphinic acid)	$H_3PO_2$	+1	White P <sub>4</sub> + alkali
Orthophosphorous acid (Phosphonic acid)	$H_3PO_3$	+3	$P_2O_3 + H_2O$
Pyrophosphorous acid	$H_4P_2O_5$	+3	$PCl_3 + H_3PO_3$
Hypophosphoric acid	$H_4P_2O_6$	+4	Red P <sub>4</sub> + alkali
Orthophosphoric acid	$H_3PO_4$	+5	$P_4O_{10} + H_2O$
Pyrophosphoric acid	$H_4P_2O_7$	+5	Phosphoric acid + heat
Metaphosphoric acid	$(HPO_3)_n$	+5	Phosphorus acid + Br <sub>2</sub> , heated in a sealed tube

#### GROUP 16 ELEMENTS (OXYGEN FAMILY)

#### **Electronic Configuration**

Element	At. No.	Electronic Configuration	Oxidation State
Oxygen (O)	8	[He] $2s^2 2p^4$	-2, -1, +1, +2
Sulphur (S)	16	$[Ne]3s^23p^4$	-2, +2, +4, +6
Selenium (Se)	34	$[Ar]3d^{10}4s^24p^4$	-2, +2, +4, +6
Tellurium (Te)	52	[Kr] $4d^{10}5s^25p^4$	-2, +2, +4, +6
Polonium (Po)	84	[Xe] $4f^{14}5d^{10}$	+2, +4, +6
		$6s^26p^4$	
Livermorium	116	[Rn] $5f^{14}6d^{10}$	
(Lv)		$7s^27p^4$	-

#### **Physical Properties**

- Atomic and ionic radii increase down the group.
- **Ionisation enthalpy** decreases down the group and is less than that of group 15 elements due to stability of half filled *p*-subshell of group 15 elements.
- Electronegativity decreases down the group.

- Electron gain enthalpy for oxygen is less negative than sulphur due to its small size. However, from sulphur onwards it again becomes less negative upto polonium.
- **Melting and boiling points** increase down the group with increase in atomic size upto Te while Po has both m.pt. and b.pt. less than Te.
- **Elemental state**: Oxygen is diatomic  $(O_2)$  due to  $p\pi p\pi$  multiple bonding. S, Se and Te exist as octa atomic  $(S_8, Se_8, Te_8)$  due to absence of  $p\pi p\pi$  multiple bonding.
- All the elements of group 16 exhibit allotropy.

#### **General Trends**

- Hydrides :
  - Bond angle and Thermal stability:
     H<sub>2</sub>O > H<sub>2</sub>S > H<sub>2</sub>Se > H<sub>2</sub>Te
  - Volatility:  $H_2S > H_2Se > H_2Te > H_2O$
  - Acidic strength and Reducing nature:
     H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te
- Halides:
  - Stability:  $SF_6 > SeF_6 > TeF_6$

#### Anomalous Behaviour of Oxygen

- Oxygen differs from the rest of the elements of oxygen family due to
  - small size
  - high electronegativity
  - non-availability of *d*-orbitals.

#### • Points of difference:

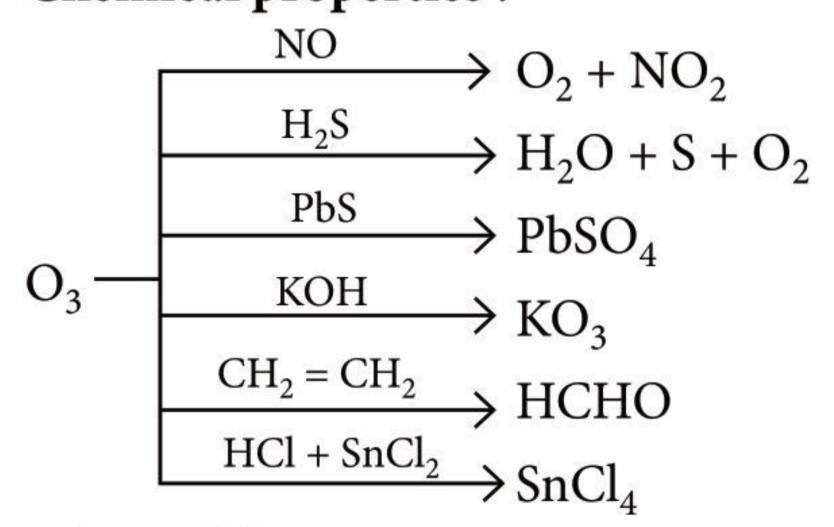
- Oxygen is a diatomic gas while others are solids.
- Oxygen exhibits oxidation states of -2, -1
   and +2 only while other members show both
   negative and positive oxidation states like -2,
   +2, +4 and +6.
- Due to high electronegativity of oxygen, hydrogen bonding is present in water.
- Oxygen is highly non-metallic due to high electronegativity.
- Oxygen is paramagnetic while others are diamagnetic.

#### Dioxygen

- Preparation:  $2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + \text{O}_2$
- Physical properties: Colourless, odourless, tasteless, sparingly soluble in water.
- Chemical properties:  $C + O_2 \rightarrow CO_2$ ;  $Pb + O_2 \rightarrow PbO_2$
- Uses: In welding and cutting, as fuel in rocket.

#### Ozone

- Preparation:  $3O_2 \rightleftharpoons 2O_3$
- Physical properties: Pale blue gas or dark blue liquid or violet black solid, strong characteristic smell.
- Chemical properties:



#### Simple oxide

 A binary compound of oxygen with other elements is oxide. It can be classified into acidic, basic, neutral, amphoteric and mixed on the basis of their reactivity.

#### **Allotropes of Sulphur**

Two allotropes of sulphur are known; yellow rhombic and monoclinic.

#### **Sulphur Dioxide**

- Preparation:  $S + O_2 \rightarrow SO_2$  $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
- **Physical properties :** Colourless gas with pungent smell.
- Chemical properties:

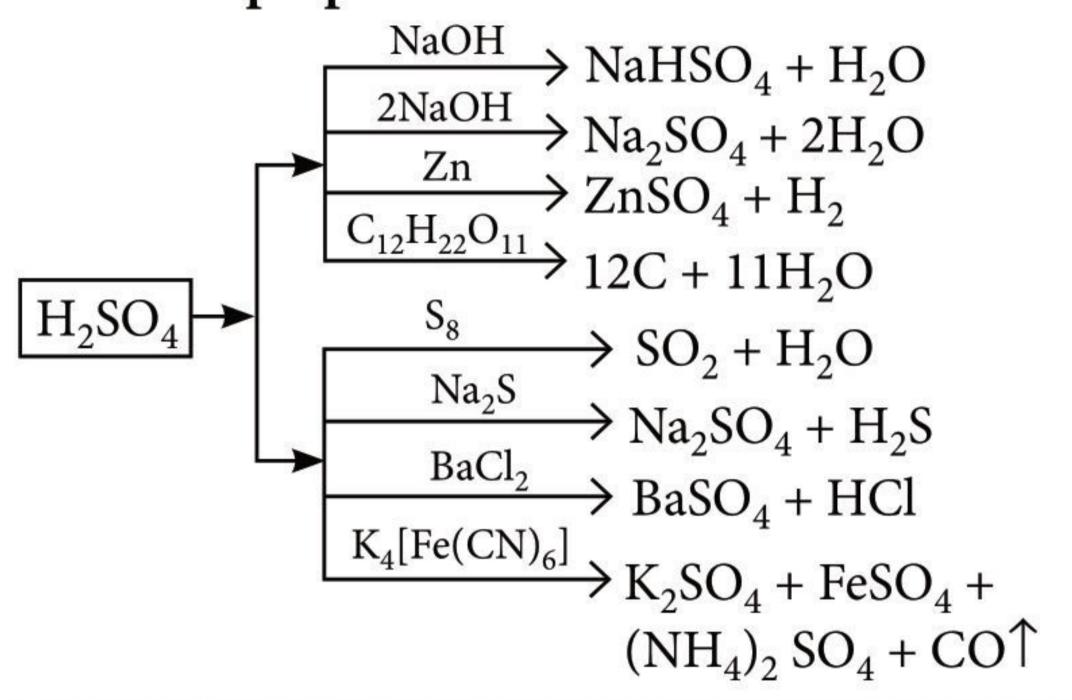
$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$
 (reaction with water)  
 $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \xrightarrow{SO_2} 2NaHSO_3$ 

• **Uses**: It is angular, used in refining petroleum and in bleaching wool.

#### **Sulphuric Acid (Oil of Vitrol)**

#### Preparation:

 $H_2O + SO_3 \rightarrow H_2SO_4$ ;  $H_2O_2 + SO_2 \rightarrow H_2SO_4$ Chemical properties:



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#### SOME IMPORTANT OXOACIDS OF SULPHUR

Oxoacid	Oxidation state, basicity and salt type	Structure	Properties
Sulphurous acid, H <sub>2</sub> SO <sub>3</sub>	$S = +4$ , dibasic, and forms two series of salts : sulphites $(SO_3^{2-})$ and bisulphites $(HSO_3^{-})$	HO O HO	<ul> <li>Acts as reducing agent as well as oxidising agent.</li> <li>Exists only in solution.</li> </ul>
Sulphuric acid, H <sub>2</sub> SO <sub>4</sub>	$S = +6$ , dibasic and forms two series of salts: sulphates $(SO_4^{2-})$ and bisulphates $(HSO_4^{-})$	HO S O OH	<ul> <li>Highly corrosive</li> <li>Acts as oxidising agent and dehydrating agent.</li> </ul>
Peroxomonosulphuric acid (Caro's acid), H <sub>2</sub> SO <sub>5</sub>	S = +6, monobasic and forms single type of salt : peroxymonosulphates (HSO <sub>5</sub> <sup>-</sup> )	O S O O O O O O O O O	<ul> <li>White, crystalline and hygroscopic solid.</li> <li>Powerful oxidising agent.</li> </ul>
Peroxodisulphuric acid (Marshall's acid), H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	S = +6 and forms single type of salt : peroxydisulphates $(S_2O_8^{2-})$		<ul> <li>Colourless, crystalline and hygroscopic solid.</li> <li>Strong oxidising agent.</li> </ul>

#### GROUP 17 ELEMENTS (HALOGENS FAMILY)

#### **Electronic Configuration**

Element	At. No.	Electronic Configuration	Oxidation State
Fluorine (F)	9	[He] $2s^2 2p^5$	-1
Chlorine (Cl)	17	[Ne] $3s^23p^5$	-1, +1, +3, +5, +7
Bromine (Br)	35	$[Ar]3d^{10}4s^24p^5$	-1, +1, +3, +5, +7
Iodine (I)	53	$[Kr]4d^{10}5s^25p^5$	-1, +1, +3, +5, +7
Astatine (At)	85	[Xe] $4f^{14}5d^{10}6s^26p^5$	<u> </u>
Tennessine (Ts)	117	$[Rn]5f^{14}6d^{10}7s^27p^5$	

#### **Physical Properties**

- Atomic and ionic radii increase down the group and halogens are smallest atoms in a period.
- Ionisation enthalpy is very high and decreases down the group.
- Electronegativity decreases down the group and fluorine is the most electronegative element.
- Electron gain enthalpy increases from F to Cl and then decreases till I. Smaller electron gain

- enthalpy of F is due to small size and interelectronic repulsions.
- **Bond dissociation enthalpy** increases from  $F_2$  to  $Cl_2$  and then decreases in  $Br_2$  and  $I_2$ . F—F bond is weaker than Cl—Cl bond because of the large repulsions of the lone pairs of  $F_2$  which are closer than in  $Cl_2$ .
- Melting points and boiling points increase down the group.

#### **General Trends**

- Oxidising power:  $F_2 > Cl_2 > Br_2 > I_2$
- Hydrogen halides:
  - **B.Pt. and M.Pt. :** HF > HI > HBr > HCl
  - Dipole moment and Thermal stability:
     HF > HCl > HBr > HI
  - Bond length, Acidic strength and Reducing nature: HF < HCl < HBr < HI

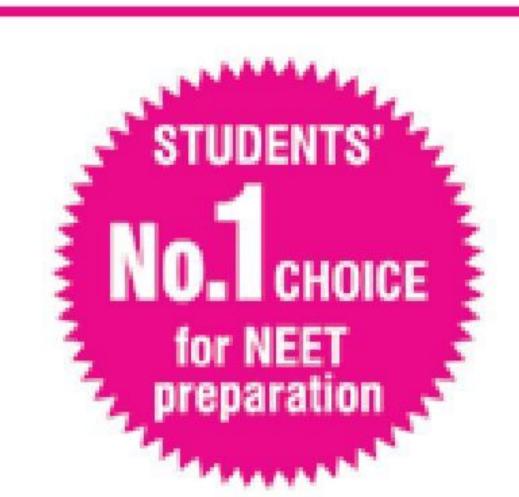
#### Oxoacids of Halogens

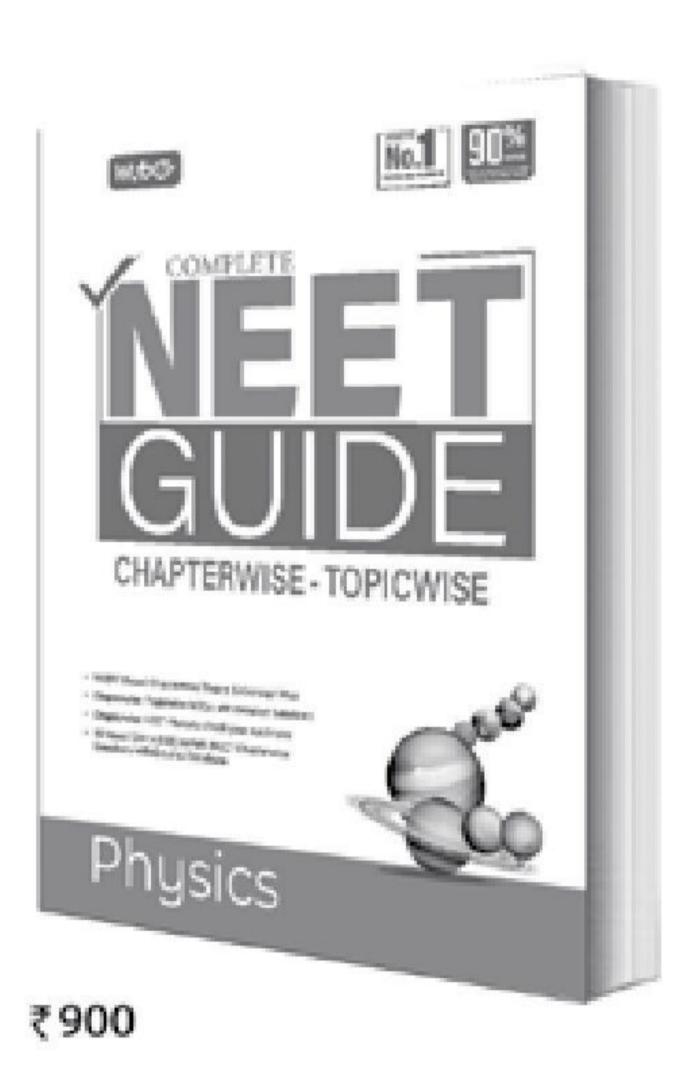
- Acidic strength:  $HClO < HClO_2 < HClO_3 < HClO_4$  HOCl > HOBr > HOI $HClO_4 > HBrO_4 > HIO_4$
- Oxidising power:  $HClO > HClO_2 > HClO_3 > HClO_4$

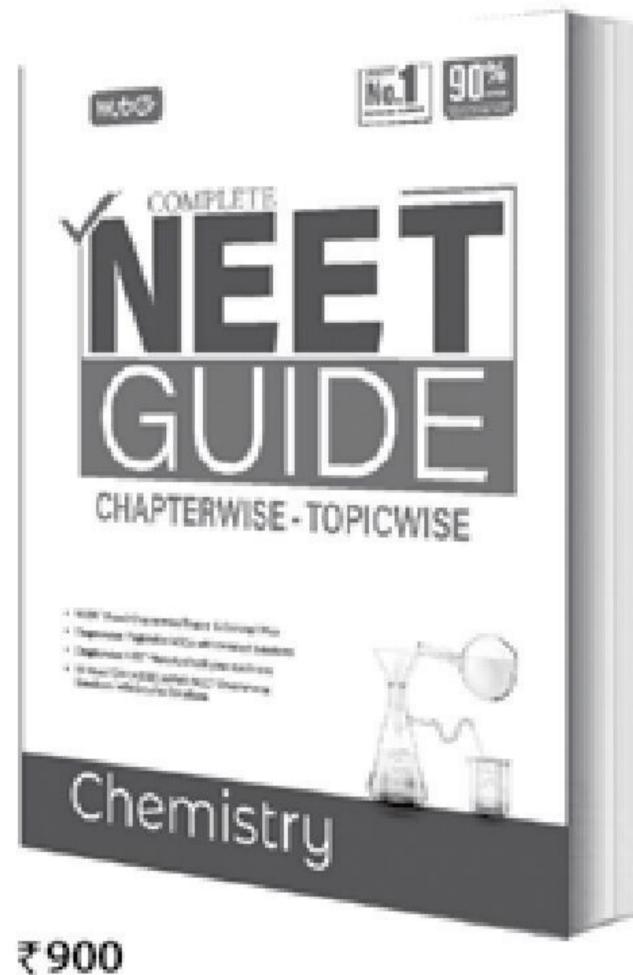
#### **Oxides**

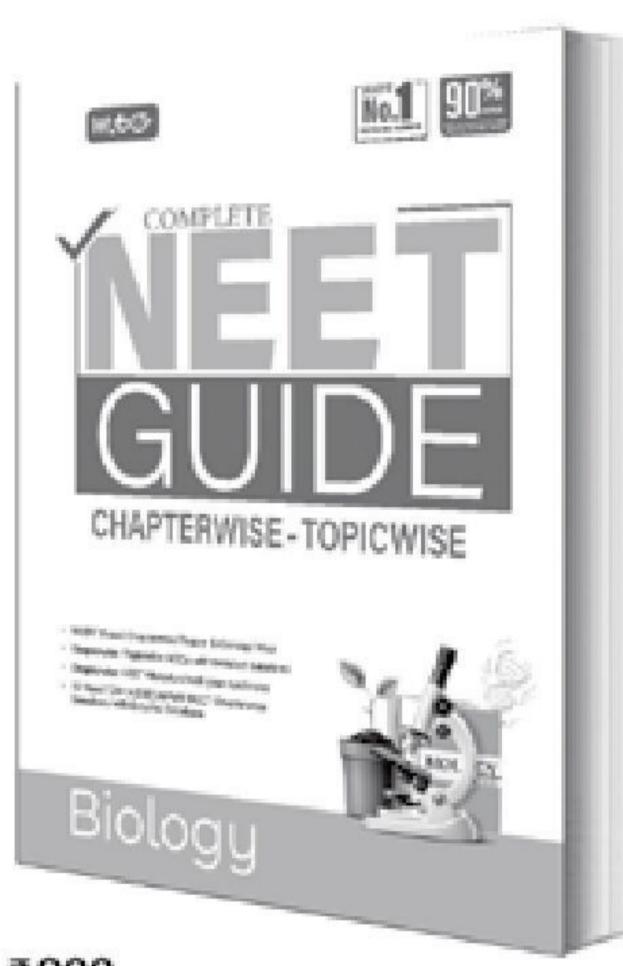
• Fluorine forms two oxides  $OF_2$  and  $O_2F_2$  called oxygen fluorides, other halogens form oxides in

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which oxidation states of these halogens range from +1 to +7.

 The higher oxides of halogens are more stable than the lower ones.

#### **Metal Halides**

- Ionic character : MF > MCl > MBr > MI
- For metals exhibiting more than one oxidation states, the halides in higher oxidation states will be more covalent than the one in lower oxidation states.

#### **Chlorine**

#### **Preparation:**

4HCl + O<sub>2</sub>  $\xrightarrow{\text{CuCl}_2}$  2Cl<sub>2</sub> + 2H<sub>2</sub>O [Deacon's process] It is also prepared by electrolysis of water.

**Physical properties :** Greenish yellow gas and pungent odour.

#### Chemical properties:

$$Cl_{2} \xrightarrow{2Na} 2AlCl_{3} \xrightarrow{H_{2}} 2HCl$$

$$Cl_{2} \xrightarrow{2Na} 2NaCl ; Cl_{2} \xrightarrow{H_{2}S} 2HCl + S$$

$$8NH_{3} \xrightarrow{2NaOH} 8NH_{4}Cl + N_{2}$$

$$Cl_{2} \xrightarrow{2NaOH} NaCl + NaOCl + H_{2}O$$

$$Cl_{2} \xrightarrow{6NaOH} 5NaCl + NaClO_{3} + 2H_{2}O$$

#### **Hydrogen Chloride**

**Preparation :** NaCl +  $H_2SO_4 \rightarrow NaHSO_4 + HCl$  **Physical properties :** Colourless and pungent smelling gas.

#### Chemical properties:

$$HCl \xrightarrow{NH_3} NH_4Cl$$

$$Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 \rightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 \rightarrow NaCl + H_2O + SO_2$$

#### **Oxoacids of Halogens**

Hypochlorous acid, chlorous acid, choloric acid and perchloric acid are some oxoacids of halogens.

#### INTERHALOGEN COMPOUNDS

Type	Hybridisation	Shape	Geometry
XX'	$sp^3$	Linear	Tetrahedral
vv′	$sp^3d$	Tahanad	Trigonal
$XX_3'$	sp a	T-shaped	bipyramidal
$XX_5'$	$sp^3d^2$	Square	Octahedral
		bipyramidal	
$XX_7'$	$sp^3d^3$	Pentagonal	Pentagonal
		bipyramidal	bipyramidal

#### GROUP 18 ELEMENTS (NOBLE GASES)

#### **Electronic Configuration**

Element	Atomic no.	Electronic configuration			
Helium (He)	2	$1s^2$			
Neon (Ne)	10	[He] $2s^2 2p^6$			
Argon (Ar)	18	[Ne] $3s^2 3p^6$			
Krypton (Kr)	36	[Ar] $3d^{10} 4s^2 4p^6$			
Xenon (Xe)	54	[Kr] $4d^{10} 5s^2 5p^6$			
Radon (Rn)	86	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$			
Oganesson (Og)	118	[Rn] $5f^{14}6d^{10}7s^27p^6$			

#### **Physical Properties**

- **Ionisation enthalpy** is very high and decreases down the group with increase in size.
- Atomic radii increase down the group.
- Electron gain enthalpy is positive as noble gases have no tendency to accept the electrons.
- Melting points and boiling points are very low due to weak interatomic dispersion forces.

#### **General Trends**

M.Pt., B.Pt., Ease of liquefaction, Solubility,
 Adsorption and Polarisability:

He < Ne < Ar < Kr < Xe

• Thermal conductivity: He > Ne > Ar > Kr > Xe

#### **Compounds of Xenon**

Compound	Structure	Preparation	Properties
XeF <sub>2</sub> (Xenon difluoride)	$F$ $Xe$ $F$ $(+2)$ Linear, $sp^3d$	$Xe + F_2 \xrightarrow{\text{Ni tube}} XeF_2$ $(2:1)$ $Xe + O_2F_2 \xrightarrow{-178^{\circ}C} XeF_2 + O_2$	$XeF_2$ $Xe + 2HF$ $H_2O$ $Xe + 2HF + \frac{1}{2}O_2$ $I_2$ $BF_3$ $2HCI$ $Xe + 2HF + Cl_2$ $Acts as fluorinating agent.$

XeF <sub>4</sub> (Xenon tetrafluoride)	F Xe  Xe $F$ $(+4)$ Square planar, $sp^3d^2$	$Xe + F_2 \xrightarrow{Ni \text{ tube}} XeF_4$ $(1:5)$ $XeF_4$	<ul> <li>Colourless, crystalline solid with melting point, 117.1°C.</li> <li>XeF<sub>4</sub> + 2H<sub>2</sub> → Xe + 4HF</li> <li>undergoes disproportionation in water.</li> <li>6XeF<sub>4</sub> + 12H<sub>2</sub>O → 4Xe + 2XeO<sub>3</sub> + 24HF + 3O<sub>2</sub></li> <li>XeF<sub>4</sub> + SbF<sub>5</sub> → [XeF<sub>3</sub>]<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup></li> <li>acts as fluorinating agent.</li> </ul>
XeO <sub>3</sub> (Xenon trioxide)	Xe $O$ $Xe$ $O$	Complete hydrolysis of $XeF_4$ and $XeF_6$ : $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 3O_2 + 24HF$ $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$	
XeOF <sub>2</sub> (Xenon oxydifluoride)	F  Xe=O $F$ $F$ $F$ $F$ $F$ $F$ $(+4)$ T-shaped, $sp^3d$	Partial hydrolysis of $XeF_4$ : $XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$	– unstable
XeO <sub>2</sub> F <sub>2</sub> (Xenon dioxydifluoride)	F $Xe$ $O$ $F$ $(+6)$ Distorted trigonal bipyramidal, $sp^3d$	Partial hydrolysis of $XeOF_4$ or $XeF_6$ : $XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$ $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$ Action of $SiO_2$ on $XeOF_4$ : $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$	<ul> <li>undergoes hydrolysis readily.</li> <li>XeO₂F₂ + H₂O → XeO₃ + 2HF</li> </ul>

XeF<sub>6</sub> cannot be stored in glass vessels because with glass, it form explosive XeO<sub>3</sub>  $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$ ;

 $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$ ;  $2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$ (from glass) (explosive)

#### **Uses of Noble Gases**

- Helium is used as breathing mixture (or oxygen dilutant) for divers.
- Mixture of  $O_2$  and He is used in the treatment of asthma.

- Neon lighting is used for advertising.
- Argon is primarily used to create an inert atmosphere in light bulbs, welding and fluorescent bulbs.
- The light emitted by krypton in an electric discharge tube is used for runway and approach lights in airports.
- Xenon is used in electrical flash bulbs for high speed photography.
- Radon is used in radiotherapy of cancer.

#### The *d*-and *f*-Block Elements

#### TRANSITION ELEMENTS (d-BLOCK ELEMENTS)

- Transition elements are the elements which lie in between *s*- and *p*-block elements in the long form of periodic table.
  - They are called d-block elements as the last electron enters in the *d*-orbital.
- General electronic configuration:  $(n-1)d^{1-10}ns^{1-2}$
- Transition series: d-block consists of four transition series,

1<sup>st</sup> Transition series or 3d series :  $_{21}$ Sc -  $_{30}$ Zn

 $2^{\text{nd}}$  Transition series or 4d series :  $_{39}\text{Y} - _{48}\text{Cd}$ 

 $3^{rd}$  Transition series or 5d series :  $_{57}$ La,  $_{72}$ Hf –  $_{80}$ Hg  $4^{\text{th}}$  Transition series or 6d series :  $_{89}$ Ac,  $_{104}$ Rf  $-_{112}$ Cn

#### GENERAL CHARACTERISTICS

**Metallic character :** Due to low, ionisation potentials and presence of vacant d-orbitals, they are metallic.

Chemical reactivity: Due to high ionisation energy, high sublimation energy and low heat of hydration, they are not reactive.

**Ionisation energy:** Only small variation in ionisation potentials due to the simultaneous increase in nuclear charge as well as screening effect.

**Magnetic properties:** The magnetic moment increases with the increasing number of unpaired electrons.

**Complex formation :** Due to presence of vacant *d*-orbitals, small size and high charge density, they form large complexes.

Catalytic properties: Due to presence of vacant *d*-orbitals and variable oxidation states, they are catalytic in nature.

**High melting and boiling points :** Due to formation of covalent bonds by overlap of partially filled *d*-orbitals, they have high m.pt. and b.pt.

**Variable oxidation states**: Due to vacant *d*-orbitals, they exhibit variable oxidation states.

**Coloured compounds :** Due to presence of unpaired electrons which undergo d-d transitions, their compounds are coloured.

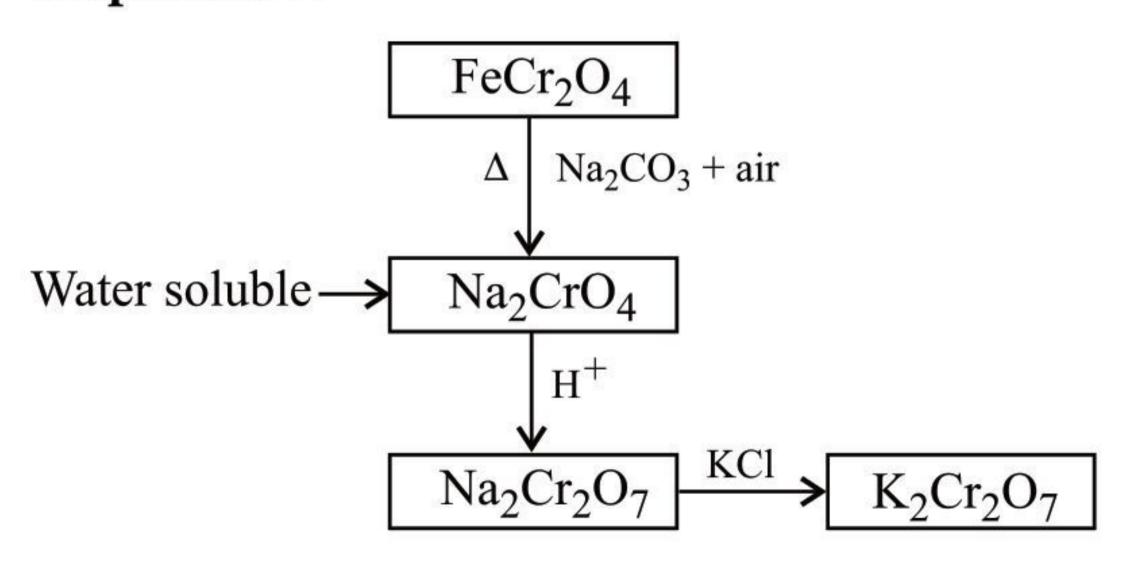
**Alloy formation :** Due to similar atomic radii, they form alloys.

**Interstitial compounds:** Due to empty spaces in their lattices in which small atoms can be accommodated, they form interstitial compounds.

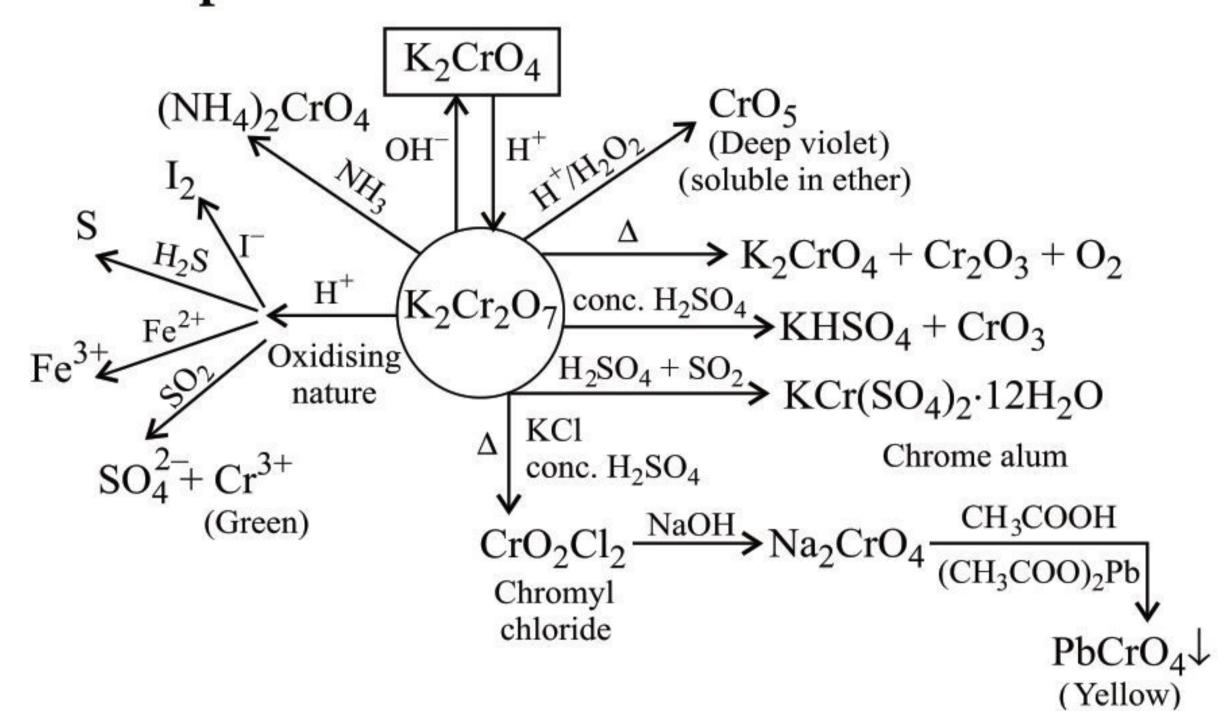
#### Some Important Compounds of Transition Elements

#### Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)

#### • Preparation:



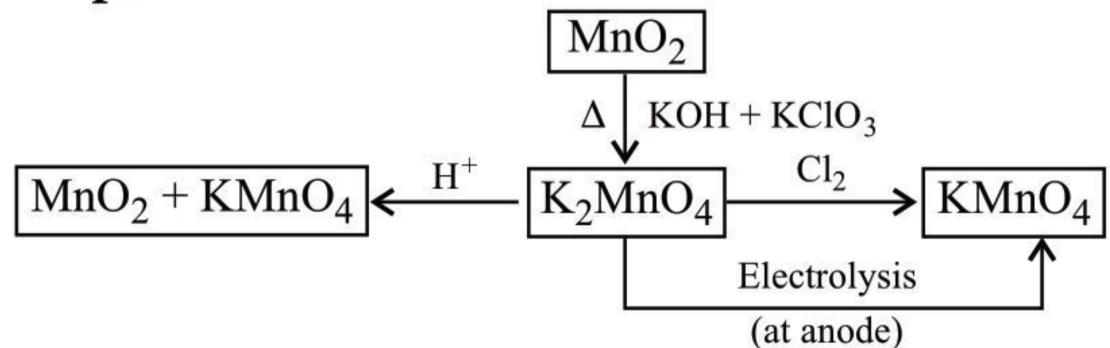
#### • Properties:



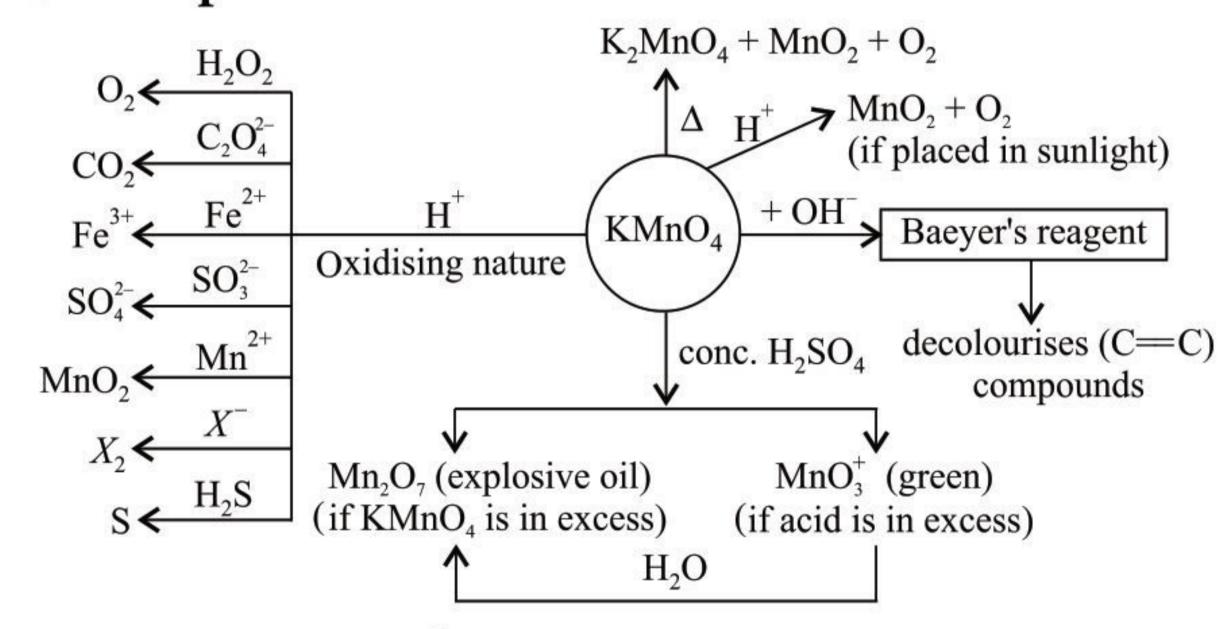
- Uses: It is used
  - in dyeing and calico printing,
  - in chrome tanning in leather industry,
  - as a volumetric reagent in laboratory for the estimation of ferrous ions, iodide ions, etc.

#### Potassium Permanganate (KMnO₄)

• Preparation:



Properties :



- Uses: It is used
  - as an oxidising agent in the laboratory and industry,
  - as a disinfectant and germicide,
  - in qualitative and quantitative analysis.

## INNER TRANSITION ELEMENTS (f-Block Elements)

• Lanthanoids: The elements with atomic numbers 58 to 71 *i.e.*, cerium to lutetium (which come immediately after lanthanum, Z = 57) are called lanthanoids.

- Actinoids: The elements with atomic numbers 90 to 103 *i.e.*, thorium to lawrencium (which come immediately after actinium, Z = 89) are called actinoids.
- They are called *f*-block elements because last electron enters into *f*-orbital.
- General electronic configuration:  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

#### **Electronic Configuration**

Element (Lantha- noids)	Electronic configuration	Element (Actinoids)	Electronic configuration
La (57)	$[Xe]5d^16s^2$	Ac (89)	$[Rn]6d^17s^2$
Ce (58)	$[Xe]4f^15d^16s^2$	Th (90)	$[Rn]6d^27s^2$
Pr (59)	$[Xe]4f^36s^2$	Pa (91)	$[Rn]5f^26d^17s^2$
Nd (60)	$[Xe]4f^46s^2$	U (92)	$[Rn]5f^36d^17s^2$
Pm (61)	[Xe] $4f^{5}6s^{2}$	Np (93)	$[Rn]5f^46d^17s^2$
Sm (62)	[Xe]4f <sup>6</sup> 6s <sup>2</sup>	Pu (94)	[Rn]5f <sup>6</sup> 7s <sup>2</sup>
Eu (63)	[Xe] $4f^{7}6s^{2}$	Am (95)	$[Rn]5f^77s^2$
Gd (64)	$[Xe]4f^{7}5d^{1}6s^{2}$	Cm (96)	$[Rn]5f^76d^17s^2$
Tb (65)	$[Xe]4f^{9}6s^{2}$	Bk (97)	$[Rn]5f^97s^2$
Dy (66)	$[Xe]4f^{10}6s^2$	Cf (98)	$[Rn]5f^{10}7s^2$
Ho (67)	$[Xe]4f^{11}6s^2$	Es (99)	$[Rn]5f^{11}7s^2$
Er (68)	[Xe] $4f^{12}6s^2$	Fm (100)	$[Rn]5f^{12}7s^2$
Tm (69)	$[Xe]4f^{13}6s^2$	Md (101)	$[Rn]5f^{13}7s^2$
Yb (70)	$[Xe]4f^{14}6s^2$	No (102)	$[Rn]5f^{14}7s^2$
Lu (71)	$[Xe]4f^{14}5d^16s^2$	Lr (103)	$[Rn]5f^{14}6d^17s^2$

#### **Lanthanoid Contraction**

- A unique feature of lanthanoids is the decrease in atomic and ionic radii from lanthanum to lutetium.
   The gradual and steady decrease across the period is called lanthanoid contraction.
- Cause of lanthanoid contraction: From La to Lu, atomic number increases, number of protons in the nucleus increases and electrons are added to 4f-orbitals which have very poor shielding power. It shields the growing nuclear charge imperfectly. As a result, effective nuclear charge increases and radius decreases.

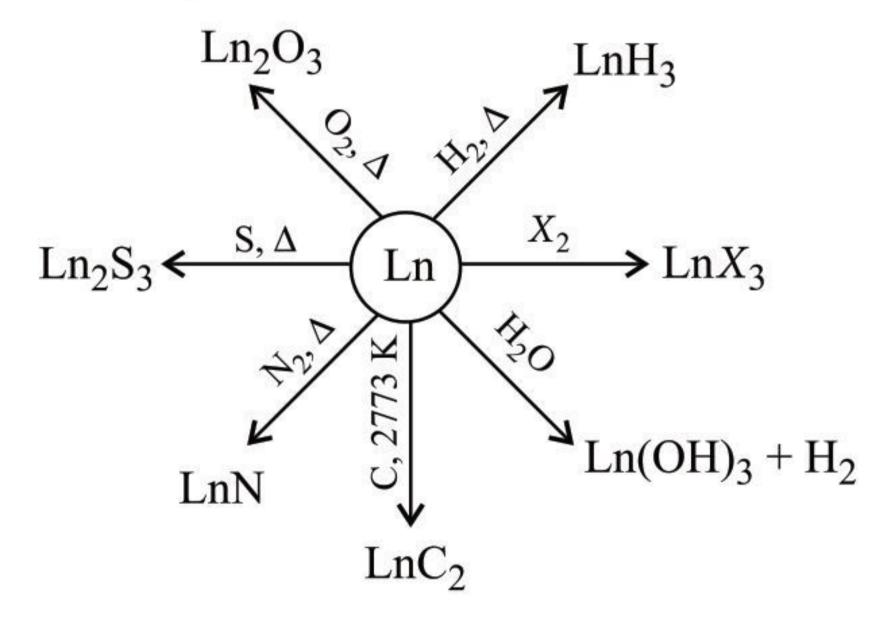
#### Consequences of lanthanoid contraction:

- Atomic radii of  $2^{nd}$  and  $3^{rd}$  transition series elements are almost identical due to lanthanoid contraction. *e.g.*, Zr = 160 pm, Hf = 159 pm. As a result, they occur in nature together, and their separation from their mixture is difficult.
- The slight difference in size of lanthanoids is responsible for difference in their properties like solubility and complex ion formation.
   This difference is utilised in their separation from the mixture of lanthanoids by solvent extraction or ion exchange.

## Differences Between Lanthanoids and Actinoids

Lanthanoids	Actinoids
These exhibit mainly +3	These also exhibit +3
oxidation state. In addition	oxidation state. In
to +3 oxidation state, the	5555
lower oxidation state of +2	( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( )
and higher oxidation state	to +7 are also noticed.
of +4 are noticed.	
These show lanthanoid	These show actinoid
contraction.	contraction.
Most ions of lanthanoids	Most ions of actinoids
are colourless.	are coloured.
These possess lesser	These possess greater
tendency for complex	tendency for complex
formation.	formation.
These do not give	These give oxocations.
oxocations.	$e.g., UO_2^{2+}$ .
Their compounds are less	Their compounds are
basic in nature.	more basic in nature.
These are not radioactive	All these are radioactive.
(only promethium shows	
radioactivity).	

#### **Chemical Properties of Lanthanoids**





#### MCQs TYPE QUESTIONS

- 1.  $P_4O_{10}$  is the anhydride of
  - (a)  $H_3PO_2$
- (b)  $H_3PO_3$
- (c)  $H_3PO_4$
- (d)  $H_4P_2O_7$
- 2. Which of the following shows nitrogen in its increasing order of oxidation number?
  - (a)  $N_2O < NO < NO_2 < NO_3^- < NH_4^-$
  - (b)  $NH_4^+ < N_2O < NO < NO_2 < NO_3^-$
  - (c)  $NH_4^+ < N_2O < NO_2 < NO_3^- < NO$
  - (d)  $NH_4^+ < NO < N_2O < NO_2 < NO_3^-$
- 3. Which of the following ions has electronic configuration [Ar] $3d^6$ ?

  - (a)  $Ni^{3+}$  (b)  $Mn^{3+}$  (c)  $Fe^{3+}$  (d)  $Co^{3+}$
- (At. nos. Mn = 25, Fe = 26, Co = 27, Ni = 28).
- 4. Which of the following is not correctly matched with the given example?
  - (a) An element of first transition series which has highest second ionisation enthalpy-Cu.
  - (b) An element of first transition series with highest third ionisation enthalpy-Zn.
  - (c) An element of first transition series with lowest enthalpy of atomisation-Zn.
  - (d) Last element of third transition series-Cd.
- 5. Which of the following statements is incorrect regarding the structure of the ClO<sub>2</sub> molecule?
  - (a) The  $ClO_2$  molecule is angular with O-Cl-Obond angle being 118°.
  - (b) The two Cl−O bonds lengths are equal.
  - (c) Both Cl—O bond lengths are greater than expected for a single Cl—O bond.
  - (d) Both Cl—O bond lengths are shorter than expected for a single Cl—O bond.
- 6. Which one of the following does not correctly represent the correct order of the property indicated against it?
  - (a) Ti < V < Cr < Mn : increasing number of oxidation states.
  - (b)  $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$ : increasing magnetic moment.
  - (c) Ti < V < Cr < Mn : increasing melting points.
  - (d) Ti < V < Mn < Cr : increasing 2<sup>nd</sup> ionisation enthalpy.

- Interstitial compounds are
  - (a) non-stoichiometric and are ionic in nature
  - (b) non-stoichiometric and are covalent in nature
  - non-stoichiometric and are neither typically ionic nor covalent in nature
  - (d) stoichiometric and are neither ionic nor covalent in nature.
- A gas (X) is obtained when copper reacts with dilute HNO<sub>3</sub>. The gas thus formed reacts with oxygen to give brown fumes of (Y). (Y) when dissolved in water gives an important acid (Z) and the gas (X). X, Y and Z respectively are
  - (a) NO;  $NO_2$ ;  $HNO_3$  (b)  $NO_2$ ; NO;  $HNO_3$
- - (c)  $N_2O$ ; NO;  $HNO_2$  (d) NO;  $N_2O$ ;  $HNO_3$
- 9. The correct order of solubility in water for He, Ne, Ar, Kr, Xe is
  - (a) He > Ne > Ar > Kr > Xe
  - (b) Xe > Kr > Ar > Ne > He
  - (c) Ne > Ar > Kr > He > Xe
  - (d) Ar > Ne > He > Kr > Xe
- 10. Assertion: Transition metals are poor reducing agents. Reason: Transition metals form numerous alloys with other metals.
  - (a) Both assertion and reason are true and reason is the correct explanation of assertion.
  - (b) Both assertion and reason are true but reason is not the correct explanation of assertion.
  - (c) Assertion is true but reason is false.
  - (d) Both assertion and reason are false.
- 11. The correct order of the thermal stability of hydrogen halides is
  - (a) HI > HBr > HCl > HF
  - (b) HF > HCl > HBr > HI
  - (c) HCl < HF > HBr < HI
  - (d) HI > HCl > HF > HBr
- 12. Which of the following is the wrong statement?
  - (a) Ozone is a paramagnetic gas.
  - (b) The two oxygen -oxygen bond length in ozone are identical.
  - (c)  $O_3$  molecule is bent.
  - (d) Ozone is violet-black in solid state.

13. Match the catalyst in column I with the process in column II and select the correction otpion.

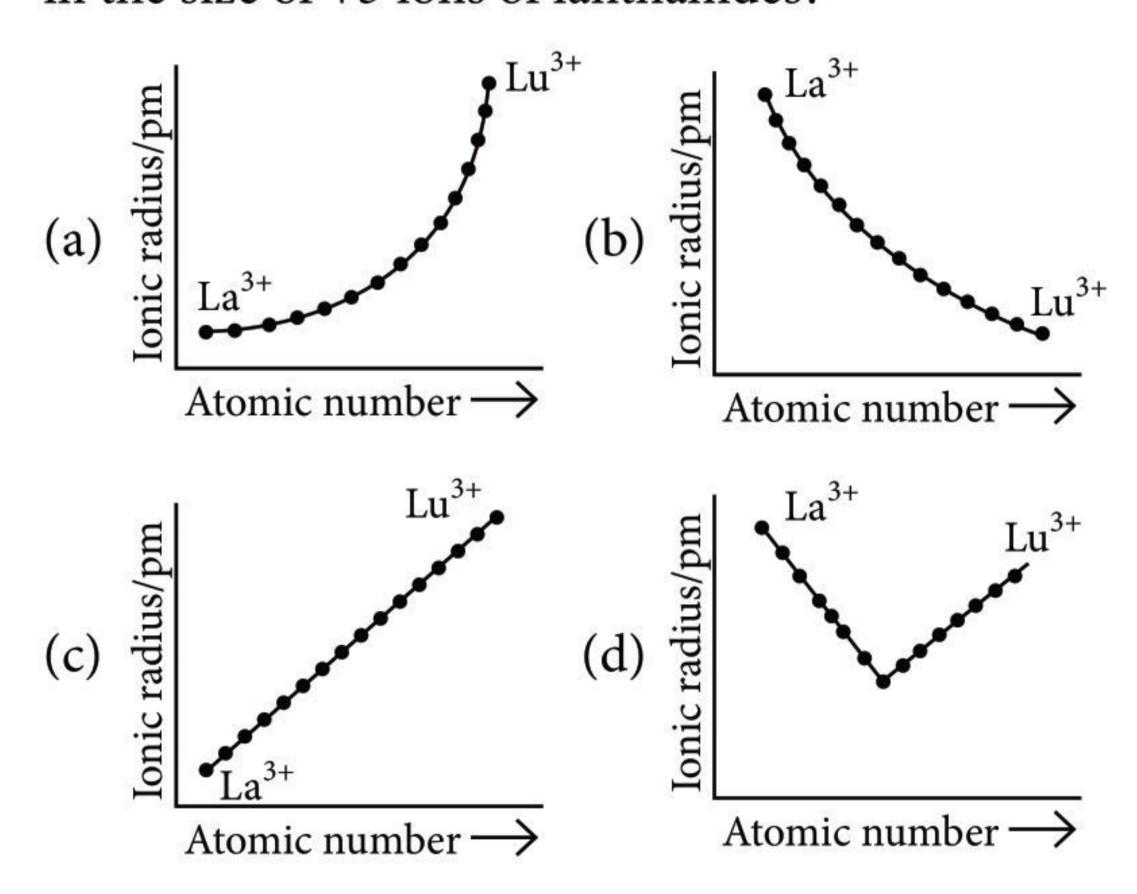
	Column I		Column II
(i)	$V_2O_5$	(p)	The oxidation of ethyne to ethanal
(ii)	TiCl <sub>4</sub> + Al(CH <sub>3</sub> ) <sub>3</sub>	(q)	Polymerisation of alkynes
(iii)	PdCl <sub>2</sub>	(r)	Oxidation of SO <sub>2</sub> in the manufacture of H <sub>2</sub> SO <sub>4</sub>
(iv)	Nickel complexes	(s)	Polymerisation of ethylene

- (a) (i)-(r), (ii)-(s), (iii)-(p), (iv)-(q)
- (b) (i)-(p), (ii)-(q), (iii)-(r), (iv)-(s)
- (c) (i)-(p), (ii)-(r), (iii)-(q), (iv)-(s)
- (d) (i)-(r), (ii)-(p), (iii)-(s), (iv)-(q)
- 14. Match the column I with column II and mark the appropriate choice.

	Column I		Column II
(A)	Laughing gas	(i)	Hydrazoic acid
(B)	Anhydride of HNO <sub>3</sub>	(ii)	Nitrous oxide
(C)	Anhydride of HPO <sub>3</sub>	(iii)	Nitrogen pentoxide
(D)	Acid hydride of nitrogen	(iv)	Phosphorus pentoxide

- (a)  $(A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)$
- (b)  $(A) \rightarrow (iv), (B) \rightarrow (i), (C) \rightarrow (ii), (D) \rightarrow (iii)$
- (c)  $(A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (iv), (D) \rightarrow (i)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (ii)
- 15. Oxygen is more electronegative than sulphur. Yet H<sub>2</sub>S is acidic while H<sub>2</sub>O is neutral. This is because
  - (a) water is a highly associated compound
  - (b) molecular mass of  $H_2S$  is more than that of  $H_2O$
  - (c) H<sub>2</sub>S is gaseous under ordinary conditions while H<sub>2</sub>O is a liquid
  - (d) H S bond is weaker than H O bond.
- 16. Identify the incorrect statement among the following.
  - (a) 4f and 5f orbitals are equally shielded.
  - (b) d-block elements show irregular and erratic chemical properties among themselves.
  - (c) La and Lu have partially filled *d*-orbitals and no other partially filled orbitals.
  - (d) The chemistry of various lanthanoids is very similar.
- 17. Assertion: Acidic character of group 16 hydrides increases from  $H_2O$  to  $H_2Te$ .

- Reason: Thermal stability of hydrides decreases down the group.
- (a) Both assertion and reason are true and reason is the correct explanation of assertion.
- (b) Both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) Assertion is true but reason is false.
- (d) Both assertion and reason are false.
- 18. An aqueous solution of a gas shows following reactions:
  - (i) It turns red litmus blue.
  - (ii) When added in excess to a copper sulphate solution a deep blue colour is obtained.
  - (iii) On addition to ferric chloride solution a brownish precipitate soluble in HNO<sub>3</sub> is obtained. Identify the gas.
- (a)  $SO_2$  (b)  $SO_3$  (c)  $NH_3$
- 19. Which of the following statements is wrong?
  - (a) Ti<sup>4+</sup> and Ag<sup>+</sup> are repelled by magnetic field.
  - (b) Mn<sup>2+</sup> shows maximum magnetic character among the first transition series.
  - (c)  $Fe^{2+}$  is more stable than  $Mn^{2+}$  towards oxidation to +3 state.
  - (d) Cr in  $Cr_2O^{2-}_7$  ion involves  $sp^3d^2$  hybridisation.
- 20. Which of the following graphs shows correct trends in the size of +3 ions of lanthanides?



#### MONTHLY TEST DRIVE CLASS XI KEY (a) (d) (a) **10**. (c) **12.** (d) **13**. (b) **15**. (d) (b) **19**. (b) **18.** (d) **17.** (d) 16. **21**. (b,c) **22**. (b,d) **23**. (a,c,d) **24**. (5) **25**. (56) **28**. (b) **29**. (c) **26**. (3) **27**. (b) **30**. (d)

#### **NUMERICAL VALUE TYPE QUESTIONS**

21. The total number of compounds having at least one bridging oxo group among the molecules given below is

N<sub>2</sub>O<sub>5</sub>, P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>7</sub>, H<sub>4</sub>P<sub>2</sub>O<sub>5</sub>, H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>

**22.** To measure the quantity of MnCl<sub>2</sub> dissolved in an aqueous solution, it was completely converted to KMnO<sub>4</sub> using the reaction,

 $MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$  (equation not balanced)

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl<sub>2</sub> (in mg) present in the initial solution is \_\_\_\_\_.

(Atomic weights in g  $\text{mol}^{-1}$ : Mn = 55, Cl = 35.5)

- 23. How many ions among the following will be coloured in an aqueous solution?

  Ti<sup>3+</sup>, V<sup>3+</sup>, Cu<sup>+</sup>, Sc<sup>3+</sup>, Mn<sup>2+</sup> and Fe<sup>3+</sup>
- 24. The number of moles of acidified KMnO<sub>4</sub> required to convert one mole of sulphite ion into sulphate ion is x/y. (x + y) is \_\_\_\_\_.
- 25. The percentage of p-character in the orbitals forming P P bonds in  $P_4$  is \_\_\_\_\_.

#### **SOLUTIONS**

- 1. (c):  $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ Orthophosphoric acid
- 2. (b):  $N_2O = +1$ , NO = +2,  $NO_2 = +4$ ,  $NO_3^- = +5$ ,  $NH_4^+ = -3$

Increasing order of oxidation state will be  $NH_4^+ < N_2O < NO < NO_2 < NO_3^-$ 

- 3. (d): The electronic configurations of the given ions are:  $Ni^{3+}$ :  $[Ar]3d^74s^0$ ,  $Mn^{3+}$ :  $[Ar]3d^44s^0$   $Fe^{3+}$ :  $[Ar]3d^54s^0$ ,  $Co^{3+}$ :  $[Ar]3d^64s^0$ Thus,  $Co^{3+}$  is the ion with the desired configuration.
- 4. (d): Hg is the last element of third transition series.
- 5. (c): Due to delocalization of electrons on three atoms, the Cl—O bond length decreases.
- 6. (c) 7. (c)
- 8. (a):  $3\text{Cu} + 8\text{HNO}_{3(\text{dil.})} \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}_{(X)}$

$$2NO + O_2 \rightleftharpoons 2NO_2$$
(X)
$$(Y)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$
(Y)
(Z)
(X)

- 9. (b): As the size of the noble gas atoms increases down the group, the polarisation of the electron cloud becomes easier. So, heavier noble gas atoms are easily polarised in polar water. Thus, solubility increases down the group.
- 10. (b) 11. (b)
- 12. (a): Ozone is diamagnetic gas.
- 13. (a) 14. (c)
- 15. (d): H−S bond is weaker than H−O bond thus, H₂S has higher tendency to release proton.
- 16. (a) 17. (b)
- 18. (c): The gas (X) is  $NH_3$ .
  - (i) Its aqueous solution is NH<sub>4</sub>OH which turns red litmus to blue.
  - (ii)  $CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4$   $Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow$   $[Cu(NH_3)_4]SO_4 + 4H_2O$ Tetrammine copper (II) sulphate (blue copper)
  - (iii)  $FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$ Brownish ppt.  $Fe(OH)_3 + 3HNO_3 \longrightarrow Fe(NO_3)_3 + 3H_2O$ Soluble
- 19. (c)
- **20. (b)**: On increasing the atomic number of lanthanoid, there is regular decrease of ionic size due to poor shielding of 4*f* electrons (lanthanoid contraction).
- 21. (5) 22. (126) 23. (4)
- 24. (7):  $2MnO_4 + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$ 2 moles 5 moles of  $SO_3^{2-} \equiv 2$  moles of  $MnO_4^-$ 1 mole of  $SO_3^{2-} \equiv 2/5$  moles of  $MnO_4^ \equiv 2/5$  moles of  $KMnO_4$ x + y = 2 + 5 = 7
- 25. (75)



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# Warm-up!

Chapterwise practice questions for CBSE Exams as per the latest pattern and reduced syllabus by CBSE for the academic session 2022-23.

Series-7

## Alcohols, Phenols and Ethers

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Time Allowed: 3 hours Maximum Marks: 70

#### GENERAL INSTRUCTIONS

General Instructions: Read the following instructions carefully.

- There are 35 questions in this question paper with internal choice.
- SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
- SECTION B consists of 7 very short answer questions carrying 2 marks each.
- SECTION C consists of 5 short answer questions carrying 3 marks each.
- SECTION D consists of 2 case-based questions carrying 4 marks each.
- SECTION E consists of 3 long answer questions carrying 5 marks each.
- All questions are compulsory.
- Use of log tables and calculators is not allowed.

#### **SECTION A**

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

- 1. Correct IUPAC name of the following compound is
  - (a) 3-phenylbutan-3-ol
  - (b) 2-phenylpropan-2-ol
  - (c) 2-phenylbutan-2-ol
- (d) 3-phenylbutan-2-ol.
- Dehydration of the following compounds in increasing order is
- (II)OH
- (III)-OH
- OH
- (a) I < II < III < IV
- II < III < IV < I
- I < III < IV < II
- none of these.
- 3. Anisole on reaction with chloromethane in presence of anhydrous AlCl<sub>3</sub> gives

- (a) *o*-methyl anisole and *p*-methoxy anisole
- (b) *p*-methyl anisole and *p*-methoxy anisole
- o-methyl anisole and p-methyl anisole
- (d) o-methoxy acetophenone and p-methoxy acetophenone.
- OH $\xrightarrow{\text{dil. HNO}_3} A$ In the given reaction,

Major product A is

 $NO_2$ 

$$(a) \bigcirc NO_2$$

$$(b) \bigcirc NO_2$$

$$OH$$

$$NO_2$$

$$OH$$

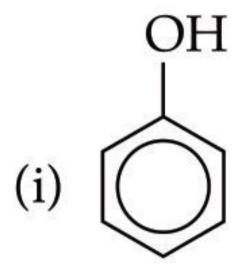
$$NO_2$$

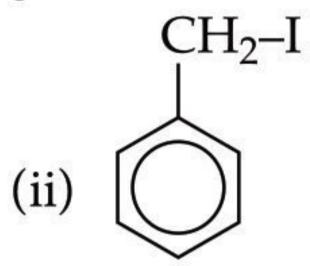
$$(c) \bigcirc NO_2$$

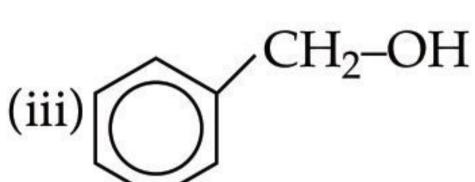
$$(d) \bigcirc NO_2$$

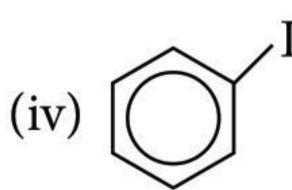
- Phenols are highly acidic compared to alcohols due to
  - the higher molecular mass of phenols
  - (b) the stronger hydrogen bonds in phenols
  - alkoxide ion is a strong conjugate base
  - (d) phenoxide ion is resonance stabilised.
- The ether that undergoes electrophilic substitution reaction is
  - (a)  $CH_3OC_2H_5$
- $C_6H_5OCH_3$
- (c) CH<sub>3</sub>OCH<sub>3</sub>
- $C_2H_5OC_2H_5$
- 7. The given ether,

when reacts with cold HI gives mixture of









- (a) (iii) and (iv)
- (i) and (ii)
- (c) (ii) and (iii)
- (i) and (iv).
- When an aqueous solution of benzene diazonium chloride is heated with dilute sulphuric acid the compound formed is
  - (a) benzene
- chlorobenzene
- (c) phenol
- (d) aniline.
- 9. Arrange the following alcohols in order of increasing reactivity towards sodium metal.
  - (i)  $(CH_3)_3C OH$
- (ii)  $(CH_3)_2CH OH$
- (iii) CH<sub>3</sub>CH<sub>2</sub>OH
- (a) (iii) < (ii) < (i)
- (b) (ii) < (i) < (iii)
- (c) (i) < (ii) < (iii)
- (d) (iii) < (i) < (ii)
- 10. Boiling point of ethyl alcohol is greater than ether due to
  - (a) van der Waals' forces (b) London forces
  - (c) polarity
- (d) hydrogen bonding.
- 11. Which of the following is an unsymmetrical ether?

  - (a)  $CH_3 O C_3H_7$  (b)  $CH_3 O CH_3$
  - (c)  $C_2H_5$ —O— $C_2H_5$  (d) All of these.
- 12. The major product of the following reaction is

$$OCH_3$$
 $conc. HBr (excess)$ 
 $heat$ 
 $CH = CH_2$ 

- (b) (a) CH<sub>2</sub>CH<sub>2</sub>Br CH<sub>2</sub>CH<sub>2</sub>Br (d) (c) Br-CHCH<sub>3</sub>
- 13. Phenol reacts with bromine in carbon disulphide at low temperature to give
  - (a) *m*-bromophenol

Br-CHCH<sub>3</sub>

- (b) *p*-bromophenol
- (c) *o*-and *p*-bromophenol
- (d) 2, 4, 6-tribromophenol.
- 14. In alcohols, oxygen atom is
  - (a)  $sp^2$ -hybridised
- (b) *sp*-hybridised
- (c)  $sp^3d$ -hybridised
- (d)  $sp^3$ -hybridised.
- 15. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion: Alcohols turn blue litmus red.

Reason: Alcohols give red colour with ceric ammonium nitrate solution.

Select the most appropriate answer from the options given below:

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.
- 16. Given below are two statements labelled as Assertion (A) and Reason (R).

**Assertion**: o-Nitrophenol is more volatile than *p*-nitrophenol.

Reason: Intramolecular hydrogen bonding is present in o-nitrophenol while intermolecular H-bonding in *p*-nitrophenol.

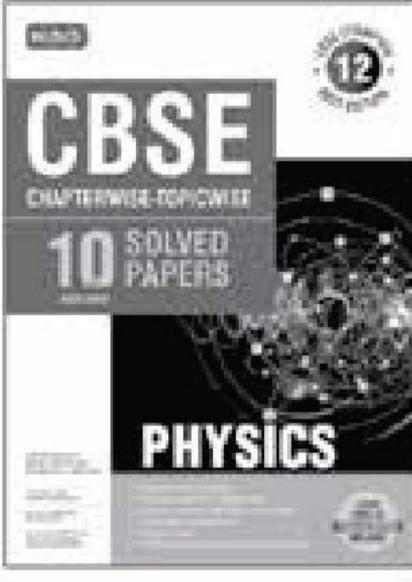
Select the most appropriate answer from the options given below:

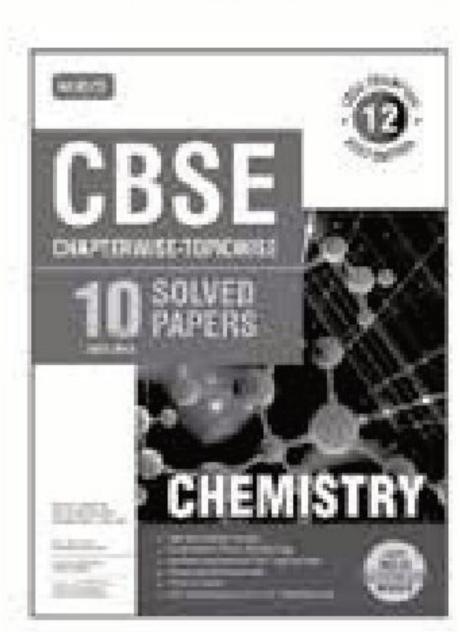
- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

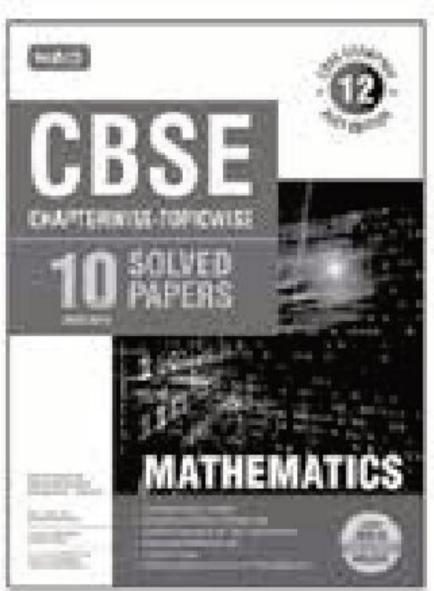


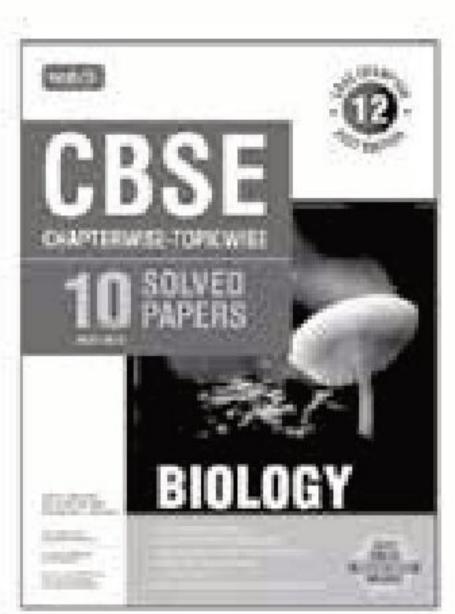


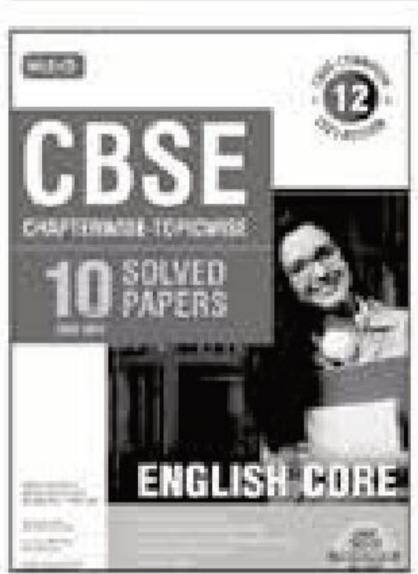
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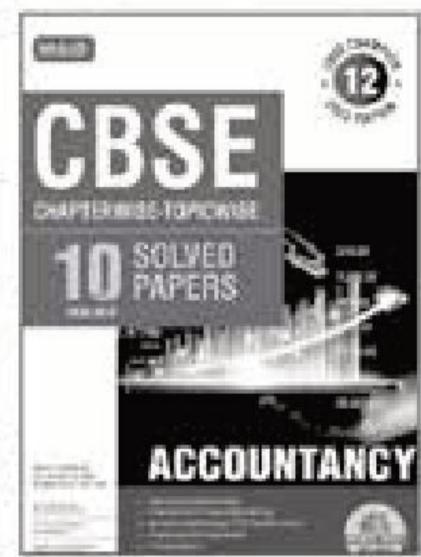


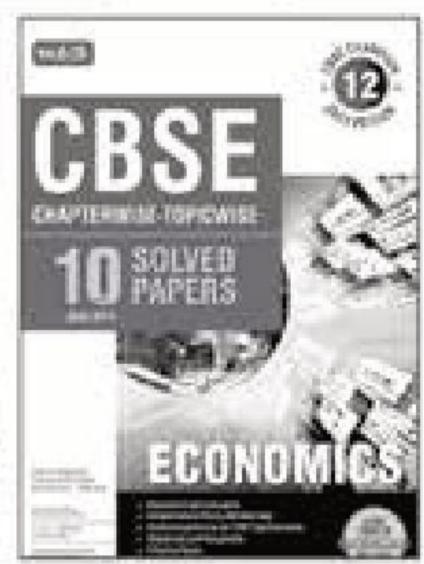


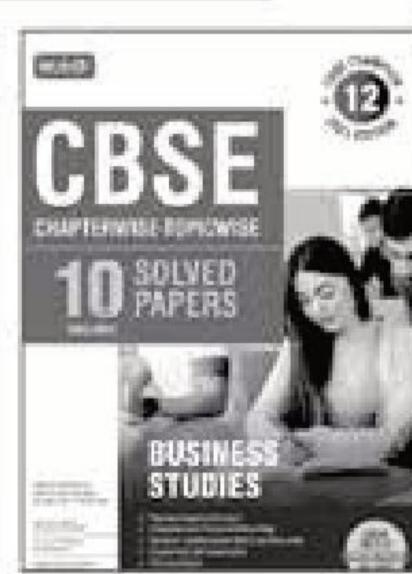


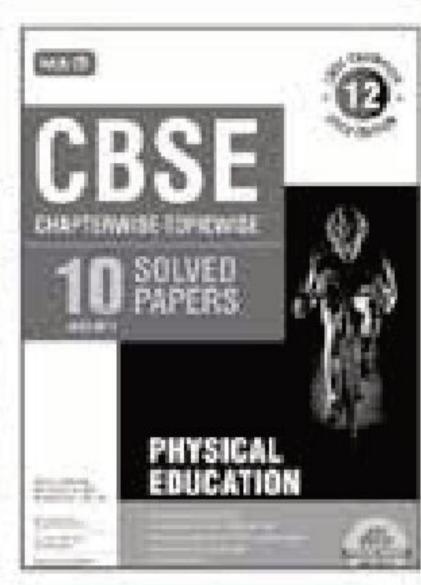




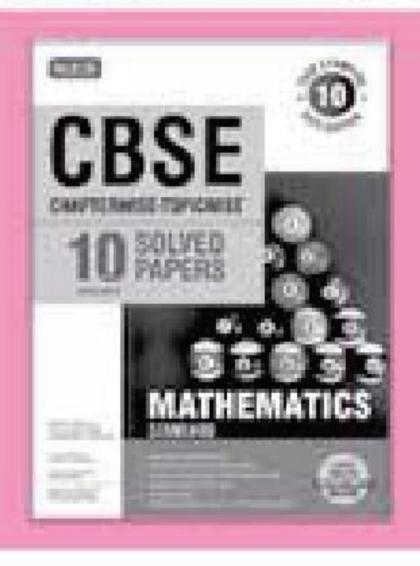




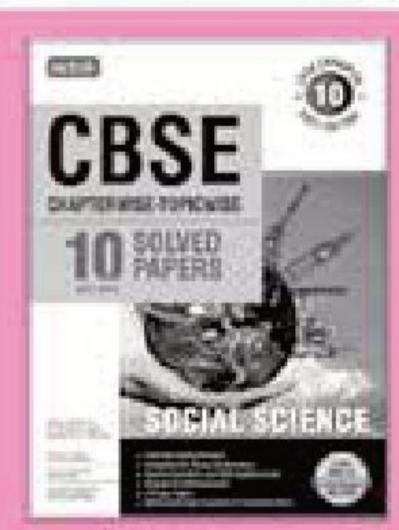


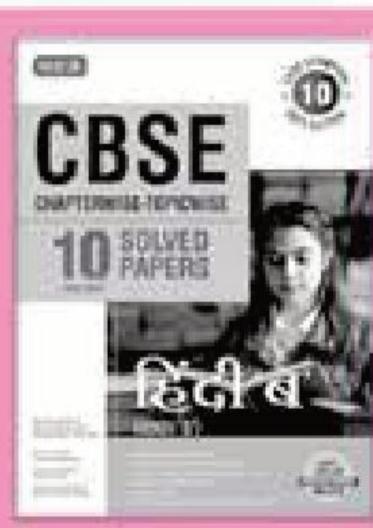












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#### HIGHLIGHTS OF 2022-23 EDITION

- Based on Reduced Syllabus
- Topicwise Graphical Analysis
- Quick Recap with Brain Map
- Previous 10 years (2022-2013) questions of CBSE
- CBSE Cognitive Level Tagging
- Key Points, Answer Tips, Concept Applied, Shortcuts, Alternating Methods, Commonly Made Mistakes provided
- CBSE Topper's Answers
- Past 3 years CBSE Sample Question Papers
- Chapterwise Self-Assessment
- 5 Practice Papers
- CBSE Sample Paper (Issued on 16th September 2022)



17. Given below are two statements labelled as Assertion (A) and Reason (R).

**Assertion**: *t*-Butyl methyl ether is not prepared by the reaction of *t*-butyl bromide with sodium methoxide.

**Reason:** Sodium methoxide is a strong nucleophile. Select the most appropriate answer from the options given below:

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.
- 18. Given below are two statements labelled as Assertion (A) and Reason (R).

**Assertion :** Dehydration of glycerol with KHSO<sub>4</sub> gives acrolein.

**Reason :** Acrolein is an  $\alpha$ ,  $\beta$ -unsaturated aldehyde. Select the most appropriate answer from the options given below:

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

#### SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

- 19. How will you convert:
  - (a) Propene to propan-2-ol
  - (b) Phenol to 2,4,6-trinitrophenol?
- 20. Write the structure of the products when butan-2-ol reacts with the following:
  - (a) CrO<sub>3</sub>
- (b) SOCl<sub>2</sub>

OR

- (a) Write the mechanism of the following reaction:  $CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$
- (b) Write the equation involved in Reimer–Tiemann reaction.
- 21. Give simple chemical tests to distinguish between the following pairs of compounds:
  - (a) Ethanol and phenol
  - (b) Propanol and 2-methylpropan-2-ol.

OR

Write the final product(s) in each of the following reactions:

- (a)  $CH_3CH_2-CH-CH_3 \xrightarrow{Cu/573 K} OH$
- (b)  $C_6H_5 OH \xrightarrow{(i) CHCl_3 + aq. NaOH} \xrightarrow{(ii) H^+}$
- **22.** Account for the following:
  - (a) Phenols do not give protonation reactions readily.
  - (b) Boiling points of phenols are higher than corresponding aryl halide, ether or arenes of comparable molecular masses.
- 23. What happens when
  - (a) ethyl alcohol reacts with red P and Br<sub>2</sub>
  - (b) oxidation of propan-1-ol occurs with alkaline KMnO<sub>4</sub> solution?
- 24. (a) How will you convert ethanol to ethoxyethane?
  - (b) What are the conditions for preparation of ethers from alcohols?
- 25. An ether would possess a dipole moment even if the alkyl groups present in it are identical. Explain.

#### **SECTION C**

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

- 26. Explain:
  - (a) The C H bond angle in alcohol is slightly less than the tetrahedral angle.
  - (b) Alcohols are highly soluble in water.
  - (c) Solubility of alcohols in water decreases with increasing size of alkyl group.
- 27. Write the product(s) of the following reactions:

(a) 
$$\xrightarrow{PCC}$$
 (b)  $\xrightarrow{COOH}$   $\xrightarrow{(CH_3CO)_2O}$   $\xrightarrow{CH_3COOH}$ 

(c)  $\xrightarrow{CH_3MgBr}$   $\xrightarrow{H_3O^+}$   $\xrightarrow{OR}$ 

- (a) Give chemical tests to distinguish between Pentan-2-ol and Pentan-3-ol.
- (b) *o*-Nitrophenol is more acidic than *o*-methoxyphenol. Explain why.
- (c) What is absolute alcohol?
- 28. Predict the products of the following reactions:

(a) 
$$CH_3 - CH = CH_2 \xrightarrow{\text{(i) } B_2H_6} \text{(ii) } 3H_2O_2/OH^-$$
?

- (b)  $C_6H_5OH \xrightarrow{Br_2(aq)}$ ? (c)  $CH_3CH_2OH \xrightarrow{Cu/573K}$ ?
- 29. (a) Phenols are stronger acids than alcohols, why?
  - (b) Draw resonance structures of phenol and phenoxide ion.
- **30.** Give reasons for **any three** of the following:
  - (a) Preparation of ethers by acidic dehydration of secondary or tertiary alcohols is not a suitable method.
  - (b) Phenylmethyl ether reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol.
  - (c) Boiling point of ethanol is higher in comparison to methoxymethane.
  - (d) Phenol does not give nucleophilic substitution reaction easily as compared to alcohols.

#### SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. Williamson's synthesis is used for the preparation of symmetrical as well as unsymmerical ethers. The reaction follows  $S_N^2$  reaction mechanism. In Williamson's synthesis, 1° alkyl halides are used for preparation of ethers because 2° and 3° alkyl halides give alkene. Ethers are cleaved by hydrogen halides to form alcohol and alkyl halide where alkyl halide corresponds to that alkyl group which has less number of carbon atoms (it is because of less steric hindrance). In polar medium, an unsymmetrical ether like tertiary butyl ethyl ether gives ethyl alcohol and tertiary butyl halide as reaction proceeds via carbocation intermediate.

#### Answer the following questions:

(a) Predict the product of the following reaction:

$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

(b) Identify the product of the following reaction:

$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

(c) Why is Williamson's synthesis not applicable to tertiary halides?

How can you convert phenol into an alkyl aryl ether?

- 32. Alcohols undergo dehydration to form alkenes on treating with a protic acid, e.g., conc. H<sub>2</sub>SO<sub>4</sub> or catalysts such as anhydrous zinc chloride or Oxidation of alcohols involves the alumina. formation of a carbon oxygen double bond with cleavage of O—H and C—H bonds. A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl. In phenol, the reaction that take place on the aromatic ring is electrophilic substitution reactions.
  - Answer the following questions:
  - (a) How do you convert ethanol to propan-2-ol?
  - (b) Why phenol undergoes electrophilic substitution more easily than benzene?
  - Write mechanism of the following reaction:

$$C_2H_5OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$$

Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.

#### SECTION E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

- 33. (a) Write the reaction and state the conditions for each of the following conversions:
  - (i) Propene to propanol.
  - (ii) Chlorobenzene to phenol.
  - (b) Write the reaction and the conditions only for the commercial preparation of phenol from cumene.

#### OR

- (a) Write chemical equations and reaction conditions for the conversion of phenol to
- (i) phenyl ethanoate (ii) ethoxybenzene. (b) How are primary, secondary and tertiary
- alcohols distinguished? UMSCRAMBILLEDWORDS

#### **NOVEMBER 2022**

- 1-d- FERMENTATION 2-i- ANTIPYRETIC
- 3-g- VULCANISATION 4-h- METALLURGY
- 6-b- CAPROLACTUM 5-a- SPELTER
- 7-j- QUENCHING 8-e- EUDIOMETER 9-f- POLYDENTATE
  - 10-c-OCCLUSION

Winner: Nisha Rawat

**34.** (a) Write the product(s) in the following reactions:

(i) 
$$CH_3$$
— $CH$ — $O$ — $CH_2$ — $CH_3$ — $HI$ — $?$  + ?  
(ii)  $CH_3$ — $CH$ = $CH$ — $CH_2$ — $OH$ — $PCC$ — $?$ ?

(ii) 
$$CH_3-CH=CH-CH_2-OH \xrightarrow{PCC}$$
?

(iii) OH 
$$(ii) \text{NaOH} \atop (iii) \text{CO}_2$$
  $(iii) \text{H}^+$ 

(b) How do you convert the following?

Phenol to anisole (ii) Aniline to phenol

- (a) Account for the following:
  - (i) Why is it that phenol is acidic and hexanol is neutral towards a solution of NaOH?
  - (ii) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of *t*-butylmethylether.
- (b) Anisole undergoes bromination with bromine and ethanoic acid even in absence of iron bromide catalyst. Why?
- 35. (a) Write the formula of reagents used in the following reactions:
  - (i) Bromination of phenol to 2,4,6-tribromophenol
  - (ii) Hydroboration of propene and then oxidation to propanol.
  - (b) Arrange the following compounds in the increasing order of their property indicated:
    - (i) p-nitrophenol, ethanol, phenol (acidic character)
  - (ii) propanol, propane, propanal (boiling point) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} ?$$

$$CH_3-CH_2-\overset{+}{O}-CH_2-CH_3+H_2O$$

#### SOLUTIONS

1. (c) 2. (a) 3. (c)

(d) 6. (b) 7. **(b)** 

8. (c): 
$$\begin{array}{c} \stackrel{+}{N} \equiv NC\overline{l} \\ +H_2O \xrightarrow{dil.H_2SO_4} \\ \stackrel{-}{\Delta} \end{array} + N_2 \uparrow + HCl \\ \text{Benzene diazonium} \\ \text{chloride} \end{array}$$

10. (d)

11. (a): Mixed or unsymmetrical ethers are those

ethers, in which both the alkyl or aryl groups attached to oxygen atom are different.

12. (c) 13. (c)

15. (d): Alcohols are weakly acidic and hence do not turn blue litmus red. Ceric ammonium nitrate test is an analytical test for alcohols. Alcohols give red colour with ceric ammonium nitrate solution.

16. (a) 17. (b)

19. (a) 
$$CH_3CH = CH_2 \xrightarrow{H_2SO_4} CH_3 - CH - CH_3$$
Propene Propan-2-ol

Picric acid (2,4,6-Trinitrophenol)

OH 
$$CrO_3$$
  $CrO_3$   $CH_3$ — $CH$ — $CH_2$ — $CH_3$   $CrO_3$   $CH_3$ — $C$ — $CH_2$   $CH_3$ 

Butan-2-ol Butan-2-one

(a) The reaction proceeds through nucleophilic substitution bimolecular (S<sub>N</sub>2) mechanism, as shown below:

Br 
$$\rightarrow$$
 H

 $C \rightarrow$  CH

 $CH_3$ 
 $H \rightarrow$ 
 $C \rightarrow$ 
 $CH_3$ 
 $H \rightarrow$ 
 $CH_3$ 

Inversion of configuration takes place during this reaction.

(b) Reimer–Tiemann reaction:

OH

CHCl<sub>3</sub>, 
$$aq \text{ NaOH}$$
 $ONa$ 

CHCl<sub>2</sub>
 $ONa$ 

CHCl<sub>2</sub>
 $ONa$ 
 $ONa$ 

OH

ONa

CHO

 $ONa$ 

CHO

 $ONa$ 

CHO

 $ONa$ 

CHO

 $ONa$ 

CHO

 $ONa$ 

CHO

 $ONa$ 

CHO

 $ONa$ 
 $O$ 

21. (a) Distinction between ethanol and phenol can be done by FeCl<sub>3</sub> test. Phenol gives a violet colouration with FeCl<sub>3</sub> solution while ethanol does not.

$$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(C_6H_5O)_6]^{3+} + 3H^+ + 3HCl$$
  
Phenol Violet colouration  
 $C_2H_5OH + FeCl_3 \longrightarrow No violet colouration$ 

**(b)** Propanol (1° alcohol) and 2-methylpropan-2-ol (3° alcohol) can be distinguished by Lucas test. With Lucas reagent (conc. HCl and anhyd. ZnCl<sub>2</sub>), 1° alcohol show no cloudiness, while 3° alcohols show cloudiness immediately.

(a) 
$$CH_3CH_2 - CH - CH_3 \xrightarrow{Cu/573 \text{ K}} CH_3CH_2 - C - CH_3 \xrightarrow{Butan-2-one} OH$$

(b)  $C_6H_5 - OH \xrightarrow{(i) CHCl_3 + aq \text{ NaOH}} CHO$ 

- 22. (a) Due to electron withdrawing effect of phenyl group, the electron density on the oxygen atom of OH group in phenols is less. Hence, phenols do not undergo protonation.
- (b) The high boiling point of phenol is mainly due to presence of intermolecular hydrogen bonding.

Salicylaldehyde

23. (a) 
$$CH_3CH_2OH \xrightarrow{Red P + Br_2} CH_3CH_2Br + H_3PO_3$$
  
Ethyl alcohol Ethyl bromide

(b) 
$$CH_3CH_2CH_2OH \xrightarrow{KMnO_4/OH^-} CH_3CH_2CHO$$

Propan-1-ol

 $CH_3CH_2COOH \xleftarrow{KMnO_4/OH^-}$ 

24. (a) 
$$CH_3CH_2OH \xrightarrow{H_2SO_4} C_2H_5-O-C_2H_5$$
  
Ethanol Ethoxyethane

- (b) Conditions for the preparation of ethers from alcohols are:
- (i) only 1° alcohol should be taken.
- (ii) alkyl group should be unhindered.
- (iii) temperature should be kept low.
- 25. Due to the bent structure of ethers and polarity of C O bond, all ethers have a net dipole moment.

$$R \checkmark^{O} \checkmark R$$

- 26. (a) The bond angle C H in alcohol is slightly less than tetrahedral angle due to the repulsion between the unshared electron pairs of oxygen.
- (b) Alcohols are soluble in water due to formation of H-bonds with water molecules. Example,

(c) Alkyl groups are hydrophobic in nature. So, as size of alkyl group increases, its solubility in water decreases.

27. (a) 
$$\xrightarrow{PCC}$$
 OH  $\xrightarrow{COOH}$  CH<sub>3</sub>CO O  $\xrightarrow{H^+}$  OCOCH<sub>3</sub>  $\xrightarrow{COOH}$  + CH<sub>3</sub>COOH  $\xrightarrow{Aspirin}$  OH CH<sub>3</sub>  $\xrightarrow{OH}$  CH<sub>3</sub>COOH  $\xrightarrow{OH}$  CH<sub>4</sub>COOH  $\xrightarrow{OH}$  CH<sub>4</sub>COOH

(a) On adding I<sub>2</sub> and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.

$$\begin{array}{c} \text{CH}_{3} - \text{CH} - \text{CH}_{2}\text{CH}_{2}\text{CH}_{3} \xrightarrow{\text{I}_{2} + \text{NaOH}} \\ \text{OH} \\ \text{Pentan-2-ol} \\ \text{Yellow ppt.} \end{array}$$

- (b) As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion by dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group destabilise the phenoxide ion by intensifying the negative charge. Thus, o-nitrophenol is more acidic than o-methoxyphenol.
- (c) 100% ethanol is known as absolute alcohol.

28. (a) 
$$CH_3$$
— $CH$ = $CH_2$  (i)  $B_2H_6$  (ii)  $3H_2O_2/OH$   $CH_3CH_2CH_2OH$ 

OH

Br

Br

2,4,6-Tribromophenol

(c) 
$$CH_3CH_2OH \xrightarrow{Cu/573 \text{ K}} CH_3CHO$$

29. (a) In alcohols, —OH group is attached to electron releasing alkyl group which decreases the polarity of O—H bond while in phenols—OH group is attached to electron withdrawing phenyl group which increases the polarity of O—H bond.

(b) (I) Resonance structures of phenol

(II) Resonance structures of phenoxide ion

**30.** (a) Acidic dehydration of 2° and 3° alcohols give alkenes rather than ethers. Due to steric hindrance, the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. The protonated 2° and 3° alcohols lose water molecules to form stable 2° and 3° carbocations.

(b) Protonation of anisole (phenyl methyl ether) gives methyl phenyl oxonium ion.

$$C_6H_5-\overset{+}{O}-CH_3$$

In this ion, the stronger bond is  $O-C_6H_5$ . Therefore, attack by I<sup>-</sup> ion exclusively breaks the weaker  $O-CH_3$  bond forming methyl iodide and phenol. The phenol formed does not react further to give aryl halides.

(c) Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole-dipole interactions.

(d) The C – O bond in phenol has some double bond character due to resonance and hence cannot be easily cleaved by a nucleophile. In contrast, the C – O bond in alcohols is a pure single bond and hence can be easily cleaved by a nucleophile.

cleaved by a nucleophile.

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3} - C - Br + Na\ddot{O} - CH_{3} \longrightarrow CH_{3}$$

$$CH_{3}$$

$$t-Butyl bromide$$

$$CH_{3} - C = CH_{2} + NaBr + CH_{3}OH$$

$$CH_{3}$$

$$2-Methyl propene$$

(b) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

Sodium *tert*-butoxide 2-Methoxy-2-methylpropane (c) In case of secondary or tertiary alkyl halides, elimination competes over substitution and product formed is alkene.

For example,

$$CH_{3}$$

$$C$$

(b) Phenols undergo electrophilic substitution reactions more easily than benzene due to strong activating effect of –OH group attached to benzene ring.

(c) 
$$CH_3 - \overset{H}{C} - \overset{H}{O} - \overset{H}{H} + \overset{H$$

Phenol

Chlorobenzene

- (b) The process of obtaining phenol from cumene is described in the following steps:
- (I) Cumene is oxidised in presence of air to form cumene hydroperoxide.

$$H_3C$$
 $CH_3$ 
 $CH_3$ 

Cumene (2-Phenylpropane)

Cumene hydroperoxide

(II) Cumene hydroperoxide is hydrolysed by dilute sulphuric acid which gives phenol and acetone.

(a) (i) 
$$OCOCH_3$$

$$+ CH_3COC1 \xrightarrow{Pyridine} + HC1$$
Acetyl chloride Phenol Phenyl ethanoate

OH ONa OCH<sub>2</sub>CH<sub>3</sub>

$$(ii) + NaOH \rightarrow OH + CH3CH2Br \xrightarrow{heat} OH + NaBr$$
Sod. Ethoxybenzene phenoxide

(b) Lucas test: Alcohols react with concentrated hydrochloric acid in presence of anhydrous zinc chloride to form alkyl halides.

$$R - OH + HCl \xrightarrow{ZnCl_2} R - Cl + H_2O$$

Three types of alcohols undergo this reaction at different rates. The rates of reaction with Lucas reagent [conc. HCl + ZnCl<sub>2</sub> (anhydrous)] follow the given order:

Tertiary alcohol > Secondary alcohol > Primary alcohol The following observations are made

- (I) If cloudiness appears immediately, the alcohol is tertiary.
- (II) If cloudiness appears within 5-10 minutes, the alcohol is secondary.
- (III) If the solution remains clear, i.e., no cloudiness is formed, the alcohol is primary.

34. (a) (i) 
$$CH_3 - CH - O - CH_2CH_3 \xrightarrow{HI}$$

OH

 $CH_3 - CH - CH_3 + CH_3CH_2I$ 

Propan-2-ol Iodoethane

(ii)  $CH_3-CH=CH-CH_2OH \rightarrow CH_3-CH=CH-CHO$ But-2-enal But-2-en-1-ol

Phenol to anisole: (i)

OH 
$$ONa^+$$
  $OCH_3$ 

Phenol  $CH_3Br$  Anisole

(ii) Aniline to phenol:

$$\begin{array}{c|c}
NH_2 & N_2^{+}Cl^{-} & OH \\
\hline
NaNO_2 + HCl & \hline
\end{array}$$

$$\begin{array}{c|c}
NaNO_2 + HCl & \hline
\end{array}$$

$$\begin{array}{c|c}
H_2O & \hline
\end{array}$$

$$\begin{array}{c|c}
Phenol
\end{array}$$
Phenol

The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus phenol loses H<sup>+</sup> ion to show acidic character.

OR

$$C_6H_5OH \longrightarrow C_6H_5O^- + H^+$$
Resonance stabilised

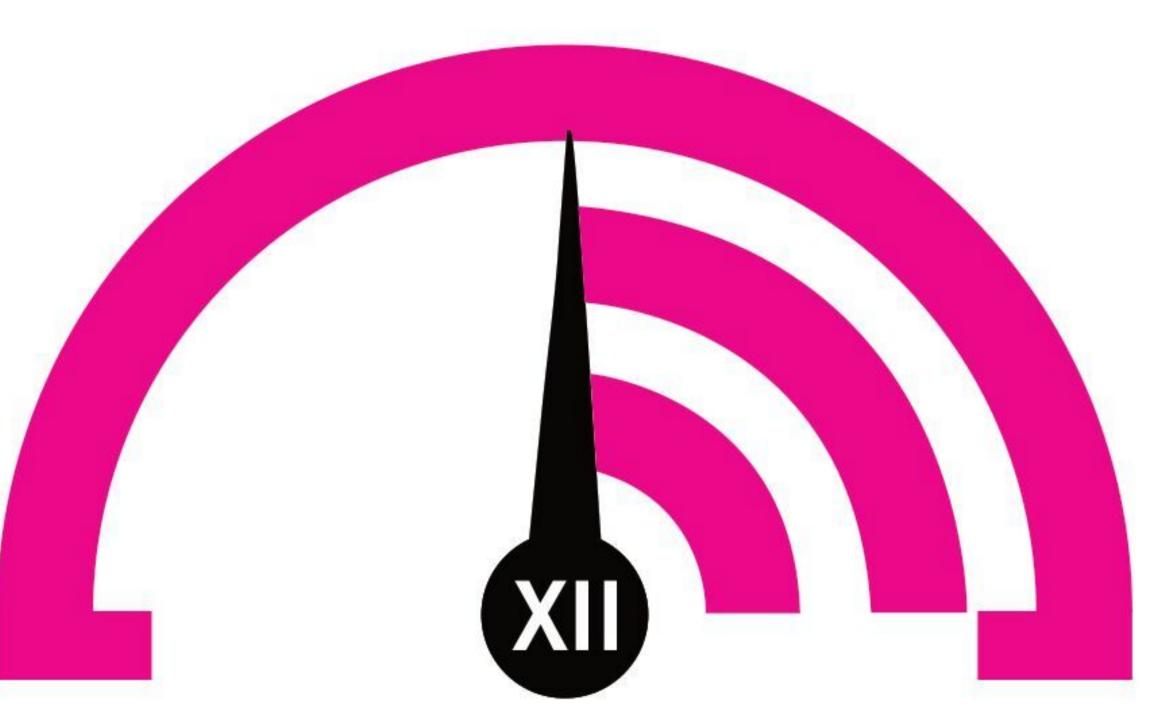
On the other hand, alkoxide ion (formed from hexanol) shows no such resonance stabilisation and is unstable.

(ii) This is because *tert*-alkyl halides undergo elimination instead of substitution.

- (b) Anisole undergoes bromination with bromine and ethanoic acid even in absence of iron(III) bromide catalyst due to activation of benzene ring by the methoxy group.
- 35. (a) (i)  $Br_2/H_2O$  (ii)  $BH_3$  in  $THF/H_2O_2$ ,  $OH^-$
- **(b)** (i) Ethanol < phenol < p-nitrophenol
  - (ii) Propane < propanal < propanol

(c) 
$$CH_3-CH_2-OH_2$$
  $CH_3-CH_2-OH_2$   $CH_3-CH_2-OH_2$   $CH_3-CH_2-OH_2-CH_3+H_2OH_3$ 

# MONTHLY TEST



his specially designed column enables students to self analyse their extent of understanding the specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

**Total Marks: 120** 

#### The Solid State | Solutions

Time Taken: 60 Min.

#### NEET

#### Only One Option Correct Type

- Which of the following statements is not correct?
  - (a) The number of carbon atoms in a unit cell of diamond is 8.
  - (b) The number of Bravais lattices in which a crystal can be categorized is 14.
  - (c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.
  - (d) Molecular solids are generally volatile.
- 2. Choose the correct statement about Henry's constant.
  - (a) Higher the value of  $K_{\rm H}$  at a given pressure, higher is the solubility of the gas.
  - (b) Higher the value of  $K_{\rm H}$  at a given pressure, lower is the solubility of the gas.
  - (c)  $K_{\rm H}$  is not a function of nature of gas.
  - (d)  $K_{\rm H}$  value for all gases is same at a given pressure.
- 3. If three elements X, Y and Z crystallise in a ccplattice with X atoms at the corners, Y atoms at the cube centre and Z atoms at the edges, the formula of the compound will be
  - (a) XYZ (b)  $XYZ_2$  (c)  $XYZ_3$  (d)  $X_2Y_2Z$
- 4. A 5.25% (w/v) solution of a substance is isotonic with a 1.5% (w/v) solution of urea (molar mass  $= 60 \text{ g mol}^{-1}$ ) in the same solvent. If the densities of both the solutions are assumed to be 1.0 g cm<sup>-3</sup>, the molar mass of the substance will be
  - (a)  $210.0 \text{ g mol}^{-1}$  (b)  $90.0 \text{ g mol}^{-1}$
- - (c)  $115.0 \text{ g mol}^{-1}$
- (d)  $105.0 \text{ g mol}^{-1}$
- 5. Which of the following statements is not correct?
  - (a) 5% aqueous solutions of NaCl and KCl are said to be isomolar.
    - (b) 1 M sucrose solution and 1 M glucose solution are isotonic.
    - (c) Molecular masses of acetic acid and benzoic acid are higher than normal mass in cryoscopic methods.

- (d) For the same concentration solution,  $\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}$ .
- Arrange the following solutions in increasing order of their osmotic pressures.
  - (i) 34.2 g/litre of sucrose
  - (ii) 60 g/litre of urea (iii) 90 g/litre of glucose
  - (iv) 58.5 g/litre of sodium chloride
  - (a) (i) < (iii) < (iv)
  - (b) (iii) < (i) < (iv) < (ii)
  - (c) (i) < (iii) < (iv) < (ii)
  - (d) (ii) < (iv) < (i) < (iii)
- What is the effect of Frenkel defect on the density of ionic solids?
  - (a) The density of the crystal increases.
  - (b) The density of the crystal decreases.
  - (c) The density of the crystal remains unchanged.
  - (d) There is no relationship between the density of a crystal and the defect present in it.
- 8. When acetone and chloroform are mixed together, which of the  $H_3C$  C = O + Cl - C - Hfollowing observations is concluded?

$$H_3C$$
  $C=O + Cl-C-H$   $H_3C$   $(A)$   $Cl$   $(B)$ 

- (a) A A and B B interactions are stronger than A - B interactions.
- (b) A A and B B interactions are weaker than A - B interactions.
- (c) A A, B B and A B interactions are equal.
- (d) The liquids form separate layers and are immiscible.
- 9. A metal of density  $7.5 \times 10^3 \text{ kg m}^{-3}$  has an fcc crystal structure with lattice parameter a = 400 pm. Calculate the number of unit cells present in 0.015 kg of the metal.
  - (a)  $6.250 \times 10^{22}$
- (b)  $3.125 \times 10^{23}$
- (c)  $3.125 \times 10^{22}$
- (d)  $1.563 \times 10^{22}$

- 10. The mole fraction of nitrogen, in a mixture containing 70 grams of nitrogen, 120 grams of oxygen and 44 grams of carbon dioxide is

- (a) 0.39 (b) 0.34 (c) 0.29 (d) 5.0
- 11. Total volume of atoms present in a fcc unit cell of a metal with radius *r* is
  - (a)  $\frac{12}{3}\pi r^3$  (b)  $\frac{16}{3}\pi r^3$  (c)  $\frac{20}{3}\pi r^3$  (d)  $\frac{24}{3}\pi r^3$
- 12. van't Hoff factor of equimolal solutions of sodium chloride, barium chloride and glucose in water are respectively
  - (a) 2, 3 and 0
- (b) 2, 3 and 6
- (c) 2, 3 and 4
- (d) 2, 3 and 1

#### **Assertion & Reason Type**

**Directions:** In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.
- 13. Assertion: Face centred cubic cell has 4 atoms per unit cell.

**Reason :** It has one atom at the corners  $\left(\frac{1}{8} \times 8 = 1\right)$  and 3 atoms at the faces  $\left(\frac{1}{2} \times 6 = 3\right)$ .

- 14. Assertion: In osmosis, movement of molecules occurs in one direction while in diffusion, movement occurs in all directions.
  - Reason: In osmosis, a semipermeable membrane is used while diffusion occurs without membrane.
- **15. Assertion**: In an ideal solution,  $\Delta_{mix}H$  is zero. **Reason :** In an ideal solution, A - B interactions are lower than A - A and B - B interactions.

#### JEE MAIN / JEE ADVANCED

#### Only One Option Correct Type

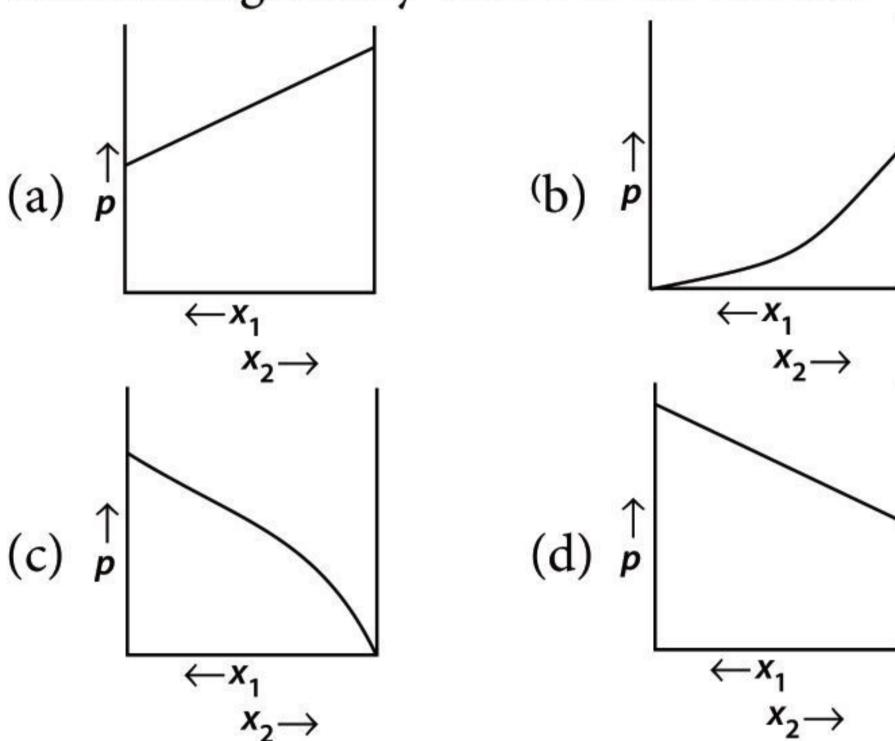
- 16. Which is not the correct statement for ionic solids in which positive and negative ions are held by strong electrostatic attractive forces?
  - (a) The radius ratio,  $r_+/r_-$  increases as coordination number increases.
  - (b) As the difference in size of ions increases, coordination number increases.
  - (c) When coordination number is eight,  $r_+/r_-$  ratio lies between 0.225 to 0.414.
  - (d) In ionic solids of the type AX (ZnS, Wurtzite), the coordination number of  $Zn^{2+}$  and  $S^{2-}$ respectively are 4 and 4.

- 17. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea is dissolved in 850 g of water. The vapour pressure of water for this solution and its relative lowering are respectively
  - (a) 23.8 mm Hg and 0.16
  - (b) 25.4 mm Hg and 0.02
  - (c) 30.2 mm Hg and 0.020
  - (d) 23.4 mm Hg and 0.017
- 18. A metal crystallises into two cubic systems, face centred cubic (fcc) and body centred cubic (bcc), whose unit cell lengths are 3.5 Å and 3.0 Å respectively. The ratio of densities of fcc and bcc is
  - (a) 1.259:1
- (b) 1:1.259
- (c) 3:2
- (d) 1.142:1
- 19. An element crystallises into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is  $24 \times 10^{-24}$  cm<sup>3</sup> and density of element is 7.2 g cm<sup>-3</sup>, the number of atoms present in 200 g of element is
  - (a)  $3.5 \times 10^{24}$  (b)  $5.7 \times 10^{23}$  (c)  $6.3 \times 10^{20}$  (d)  $1 \times 10^{10}$

#### More than One Option Correct Type

- 20. Which of the following is not true about the voids formed in 3 dimensional hexagonal close packed structure?
  - (a) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer.
  - (b) All the triangular voids are not covered by the spheres of the second layer.
  - (c) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap.
  - (d) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer.
- 21. Relative lowering of vapour pressure is a colligative property because
  - (a) it depends on the concentration of a nonelectrolyte solute in solution and not on the nature of the solute molecules
  - (b) it depends on number of particles of electrolyte solute in solution and not on the nature of the solute particles
  - (c) it depends on the concentration of a nonelectrolyte solute in solution as well as the nature of the solute molecules

- (d) it depends on the concentration of an electrolyte or non-electrolyte solute in solution as well as the nature of solute molecules
- **22.** Which statements is/are true about *hcp* and *ccp* lattice?
  - (a) Number of tetrahedral voids are twice of octahedral voids.
  - (b) 12 tetrahedral and 6 octahedral voids are present in one *hcp* unit cell.
  - (c) C.N. of *hcp* unit cell is 12.
  - (d) If an atom of tetrahedral voids displaces into octahedral voids, then it is a Schottky defect.
- 23. For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the curves?



#### Integer / Numerical Value Type

- 24. The edge length of a face centred cubic cell of ionic substance is 508 pm. If the radius of the cation is 110 pm, then the radius of the anion is \_pm.
- 25. Calculate (in gram) the amount of CaCl<sub>2</sub> (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C.
- 26. The Henry's law constant for solubility of N<sub>2</sub> gas in water at 298 K is  $1 \times 10^5$  atm. The mole fraction of N<sub>2</sub> in air is 0.8. The number of moles of N<sub>2</sub> from air dissolved in 10 moles of water at 298 K and 5 atm pressure is  $x \times 10^{-4}$ . Then the value of x is

#### **Comprehension Type**

Dissolution of solids in water can be exothermic or endothermic process but gases always dissolve in water with the evolution of heat. Dissolution of a

substance in water can be either because of ion-dipole interactions or by hydrogen bond formation. Pressure plays a significant role in the solubility of gases in water. Solubility of a gas in terms of mole fraction (x) and is related to pressure (p) according to the mathematical relation,  $p = K_{\rm H}x$ .

- 27. The value of  $K_{\rm H}$  for  $N_2$  gas in water at 298 K is 86.76 kbar, the value of  $K_{\rm H}$  for  $N_2$  in water at 303 K (in kbar) is
  - (a) 86.76
- (b) > 86.76
- (c) < 86.76
- (d) unpredictable.
- 28. Solubility of KCl in water increases with the rise in temperature. This means that  $\Delta_{diss}H$  of KCl in water is
  - (a) 0
- (b) < 0
- (c) > 0
- (d) unpredictable.

#### **Matching Type**

29. Match the column I with column II and select the correct option.

(	Column I Position of atom)	(Co	Column II (Contribution of atom per unit cell)				
(A)	Corner	(i)	1				
(B)	Edge	(ii)	1/8				
(C)	Face centre	(iii)	1/4				
(D)	Body centre	(iv)	1/2				

- (a)  $(A) \rightarrow (ii), (B) \rightarrow (i), (C) \rightarrow (iii), (D) \rightarrow (iv)$
- (b) (A)  $\to$  (ii), (B)  $\to$  (iii), (C)  $\to$  (iv), (D)  $\to$  (i)
- (c)  $(A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iv), (D) \rightarrow (iii)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (iv), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (ii)
- 30. Match the column I with column II and select the correct option.

	•					
	Column I	Column II				
(A)	$\Delta H_{\rm mix} = 0$ , $\Delta V_{\rm mix} = 0$	(i)	Non-ideal solution			
(B)	$\Delta H_{\rm mix} \neq 0$ , $\Delta V_{\rm mix} \neq 0$	(ii)	Positive deviation			
(C)	$\Delta H_{\rm mix}$ < 0, $\Delta V_{\rm mix}$ < 0	(iii)	Ideal solution			
(D)	$\Delta H_{\rm mix} > 0$ , $\Delta V_{\rm mix} > 0$	(iv)	Negative deviation			

- (a)  $(A) \rightarrow (i), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (iv)$
- (b) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (i), (C)  $\rightarrow$  (iv), (D)  $\rightarrow$  (ii)
- (c)  $(A) \rightarrow (ii), (B) \rightarrow (iii), (C) \rightarrow (iv), (D) \rightarrow (i)$
- (d) (A)  $\rightarrow$  (iii), (B)  $\rightarrow$  (ii), (C)  $\rightarrow$  (i), (D)  $\rightarrow$  (iv)

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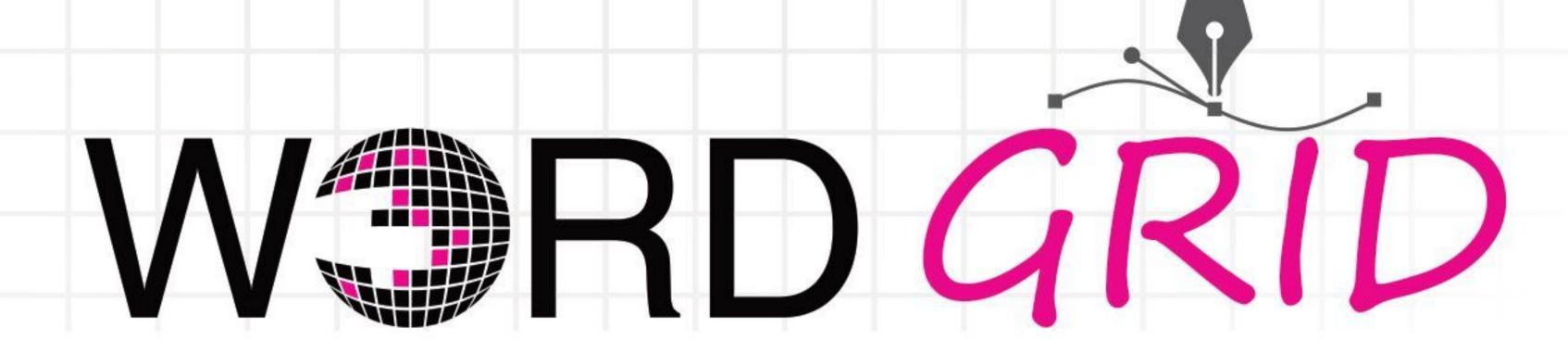
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Find and encircle the words in the given grid, running in one of the possible directions; horizontal, vertical or diagonal by reading the clues given below.

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Ν	Α	S	U	G	1	М	J	K	Н	J	Μ	Q	S	0	S
М	С	1	N	Α	D	F	Е	L	Μ	Α	R	А	F	Р	U
L	S	Μ	Τ	L	U	V	Z	Ν	Ν	D	1	S	J	C	R
Υ	U	E	С	L	T	W	Н	М	Т	В	S	Р	Т	Q	F
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R	Z	0	М	Р	0	K	Е	R	S	D	Е	1	T	Z	N
F	М	Н	S	Е	1	U	Q	Р	U	Н	Υ	В	Χ	G	Т
J	Υ	Р	V	L	Q	Χ	G	J	W	L	Т	N	0	Н	С

#### Clues

- Any of two or more physical forms in which an element can exist.
- A process in which a solid, especially a metal, is eaten away and changed by a chemical action.
- A chemical reaction in which a ferment causes an organic molecule to split into simpler substances, especially the anaerobic conversion of sugar to ethyl alcohol by yeast.
- Element with a different number of neutrons than standard.
- The clumping of particles in order to settle down impurities; often induced by chemicals such as lime or alum.
- The branch of chemistry concerned with the chemical effects of light and other electromagnetic radiations.
- A surface-active substance, such as a detergent or soap, that lowers the surface tension of a solvent (usually water).
- Elements whose properties are intermediate between those of metals and solid non-metals or semiconductors.

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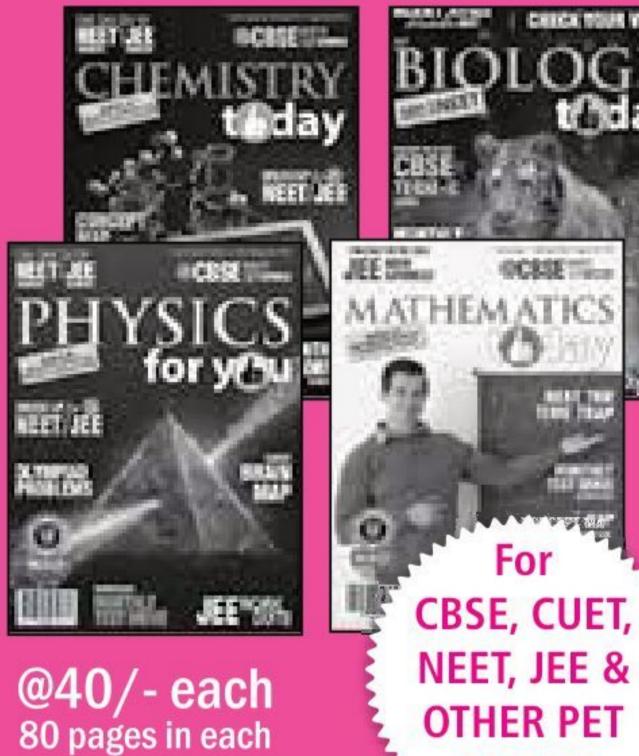


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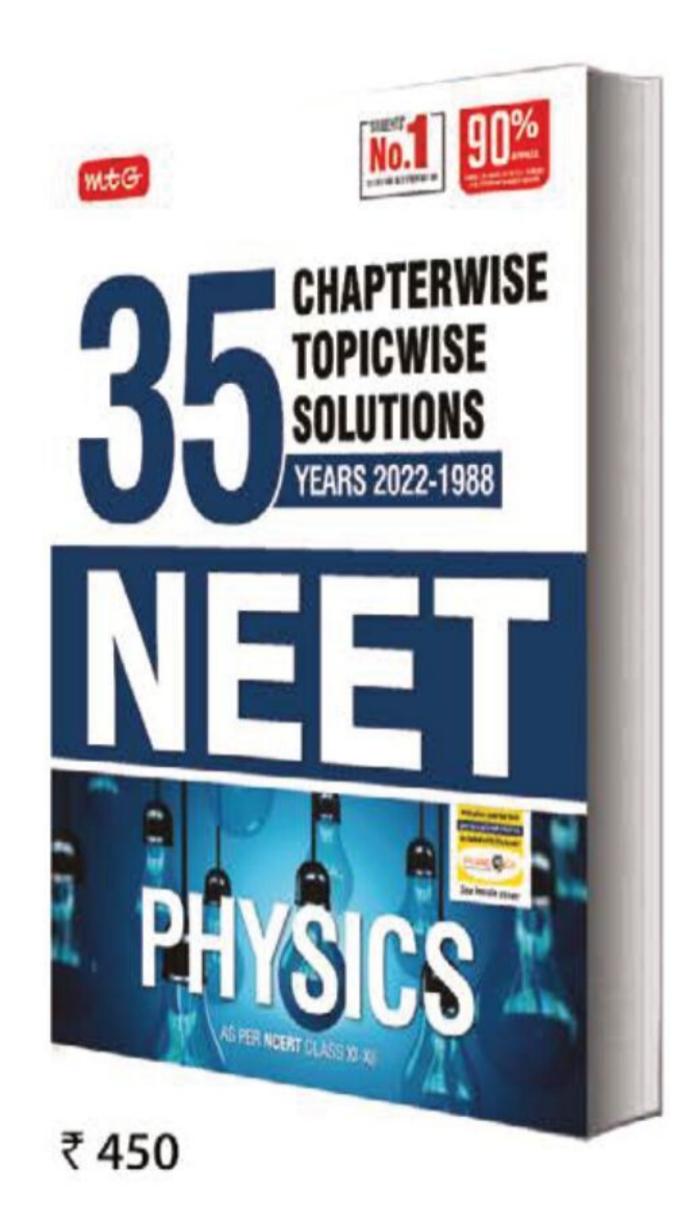


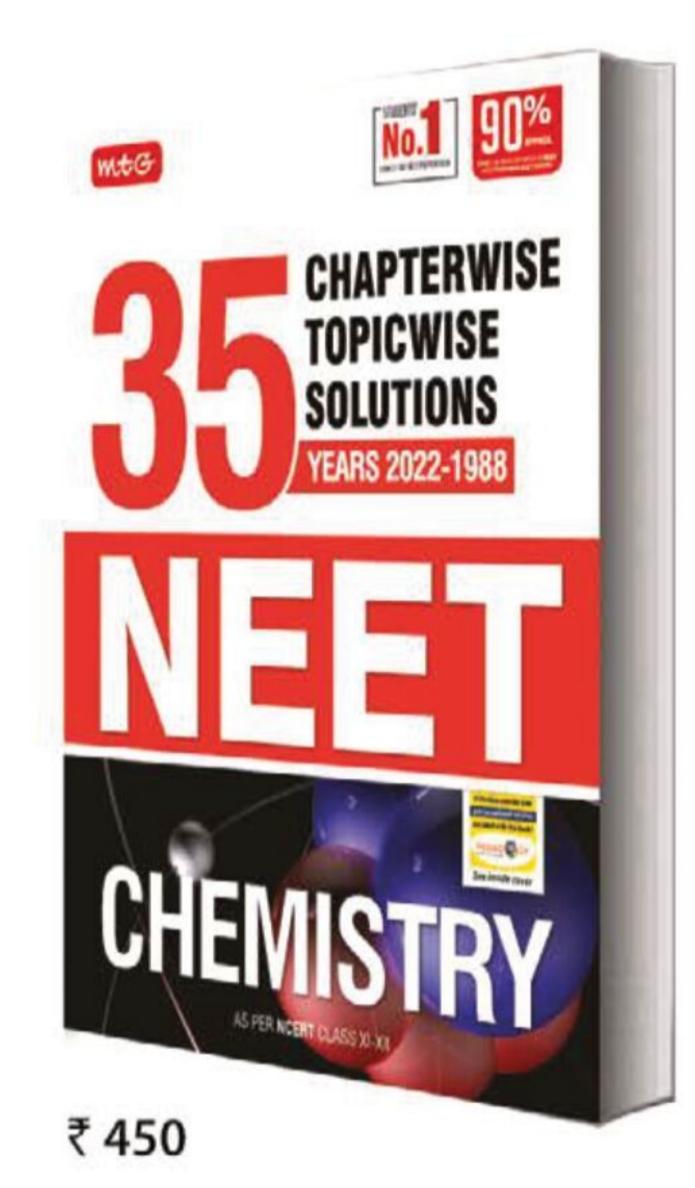
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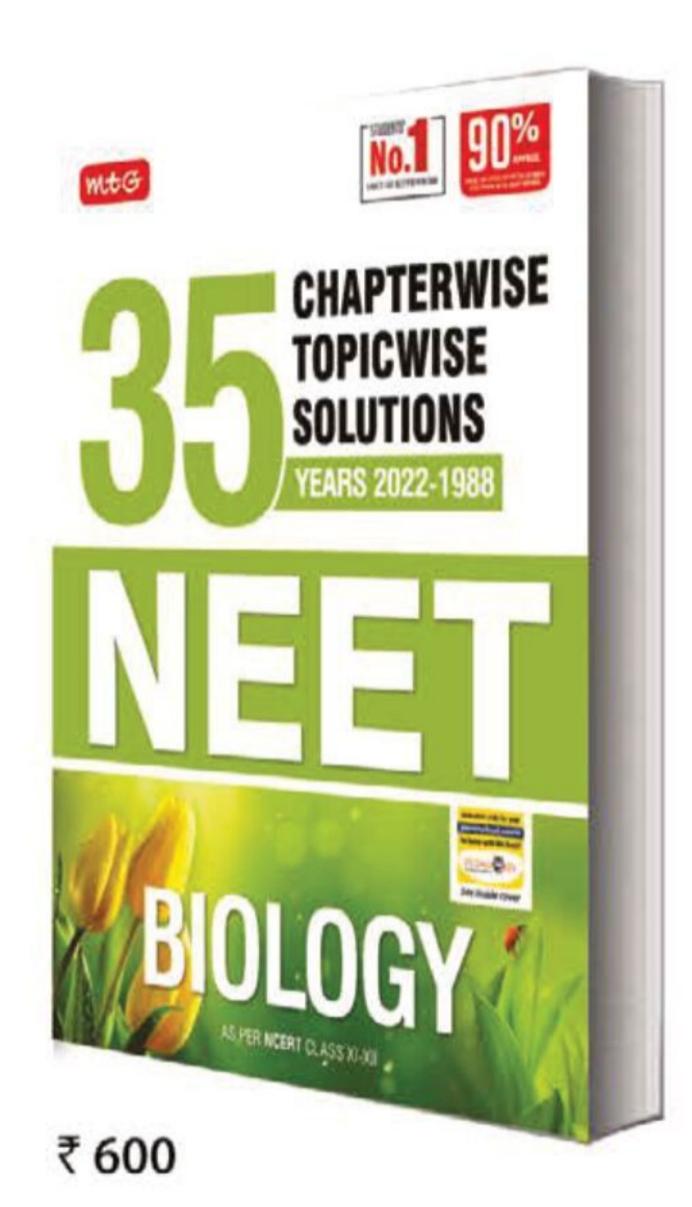
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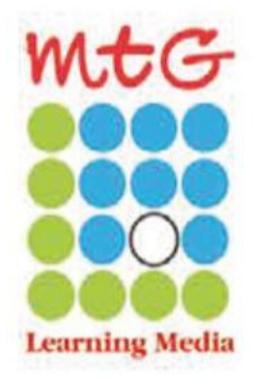
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#### HIGHLIGHTS:

- Chapterwise-Topicwise questions of last 35 years' (2022-1988) of **NEET/AIPMT**
- Chapterwise-Topicwise segregation of questions to help you assess the level of effort required to succeed
- An unmatched question bank series with close to 1,000 pages having detailed solutions by experts

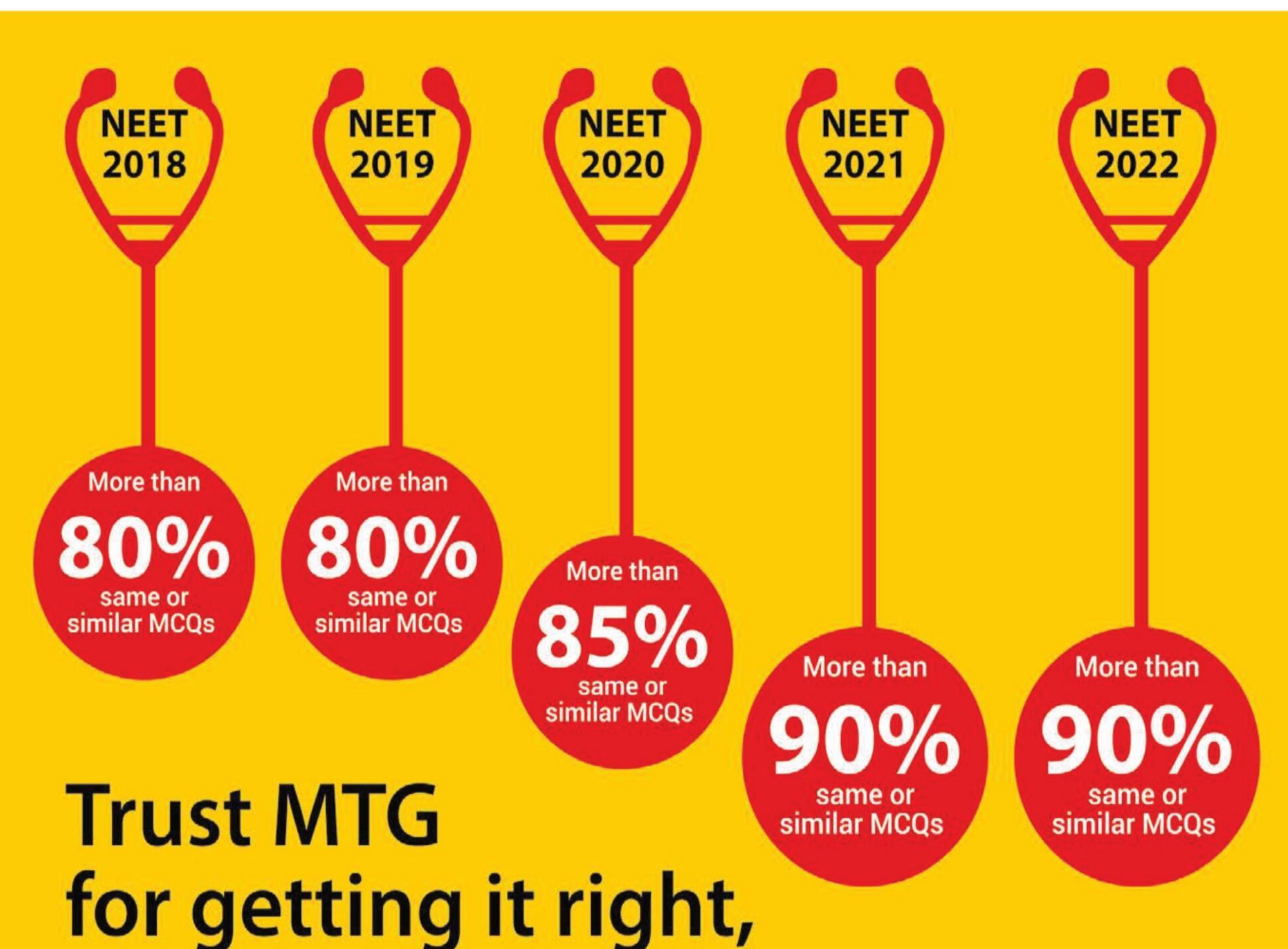


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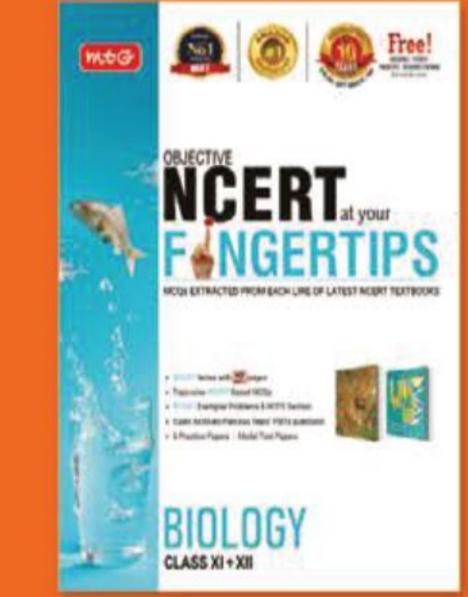
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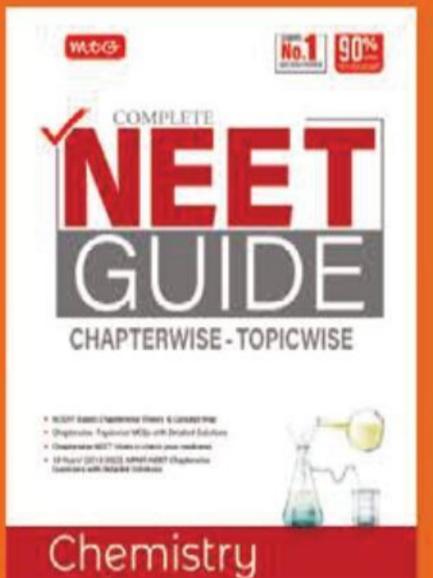
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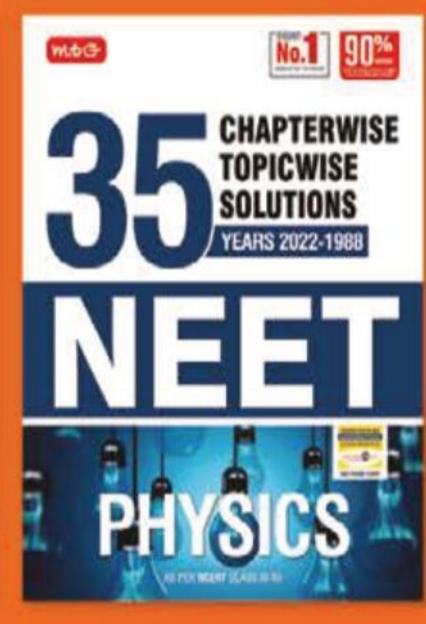
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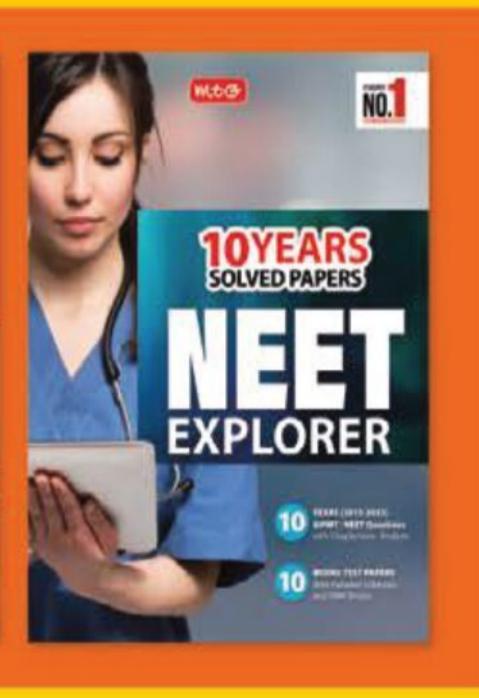














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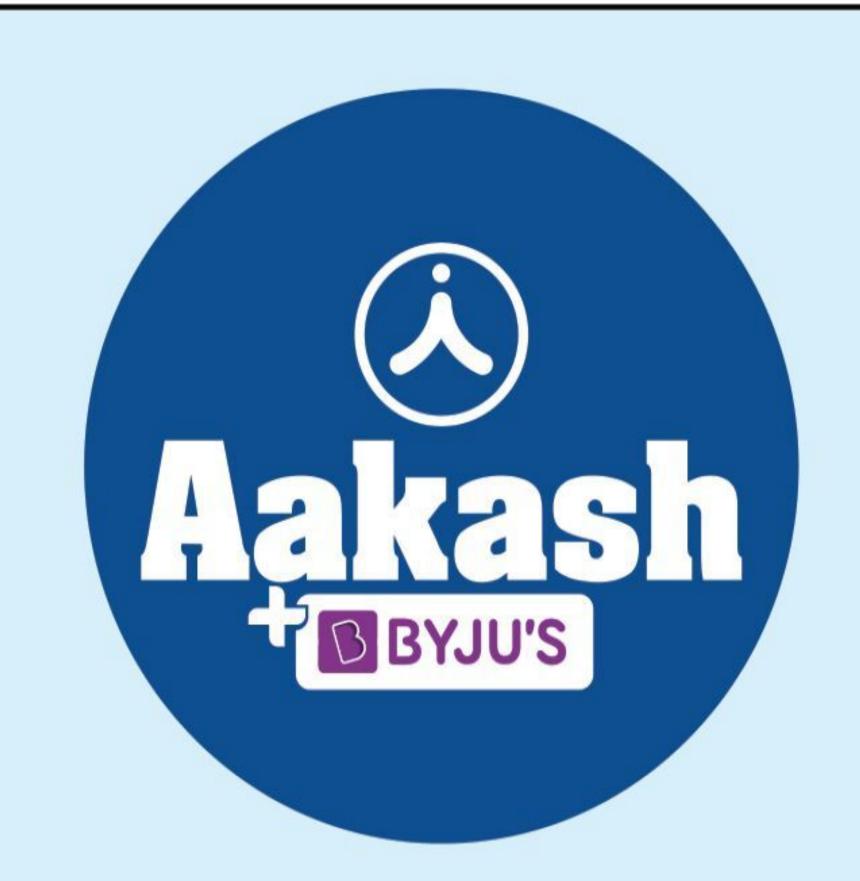






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